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FUEL-CELL PROPULSION FOR SMALL MANNED SUBMERSIBLES .

by

10) JAMES MAX/HADDOCK

B.S., University of Washington (1971)

SUBMITTED IN PARTIAL FULFILLMENT
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and

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FUEL-CELL PROPULSION FOR SMALL MANNED SUBMERSIBLES

bу

JAMES MAX HADDOCK

Submitted to the Department of Ocean Engineering on May 12, 1979 in partial fulfillment of the requirements for the degrees of Ocean Engineer and Master of Science in Naval Architecture and Marine Engineering

ABSTRACT

This thesis investigates the applicability of present fuel cell systems to small manned submersibles. A general review covers the history of submarine power systems and of research submersibles, important considerations in submersible power system design, alternative energy sources, and the basic principles and development of the chemical fuel cell. Three modern fuel cell systems for submarine use are examined in some detail, and the impact of replacing the lead-acid battery system of the 24 ton submersible, Sea Cliff, with a current hydrogen-oxygen fuel cell is assessed.

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INTRODUCTION

In the past two decades, small research and industrial submarines have performed an increasing variety of important underwater tasks. These "submersibles" as they have come to be called, have traditionally been powered by re-chargable storage batteries. Generally, battery systems provide a low cost, reliable energy source which will continue to see wide application in submersible systems; however, due to the low energy density of present batteries, many submersible missions are energy limited.

The electrochemical fuel cell is one of many advanced systems proposed for submersible power. In 1978, a United Technologies Corporation fuel cell system, evolved from space technology, was installed on a 50 ton submersible, the Deep Quest, which is currently undergoing tests off San Diego, California.

The purpose of this study is to evaluate the present applicability of fuel cell energy systems to manned submersibles of 50 tons (dry weight) and smaller. Chapter I will define the term submersible as it is used here, examine the development of underwater propulsion systems and of manned submersibles, and survey present power plant installations. Chapter II will review important design considerations for submersible power systems and survey alternative energy sources in light of current technology. In

Chapter III, fuel cells will be examined in general, and some systems applicable to submersibles will be inspected in detail. Finally, in Chapter IV, the impact of replacing the lead-acid batteries aboard the U.S. Navy's <u>Sea Cliff</u>, a submersible approximately three times smaller than <u>Deep Quest</u>, with a "state-of-the-art" fuel cell system will be assessed.

CHAPTER I

SUBMERSIBLES AND SUBMERSIBLE POWER SYSTEMS

A. Definition of "Submersible"

Although the word "submersible" is defined in Webster's Collegiate Dictionary only as "something that is submersible", it has acquired a more exact meaning among ocean scientists and engineers, offshore oil workers, and seamen. Generally, a submersible is a submarine that is designed for surveying, scientific research, salvage, rescue, and/or underwater engineering.

For the purposes of this study, the term submersible will be used to mean a manned, self-propelled underwater vehicle with an enclosed pressure hull that is not designed for a strictly military mission. This more limited definition excludes open, SCUBA supported diver delivery vehicles and unmanned, tethered submersibles such as the U.S. Navy's CURV vehicles.

Additionally, the term "small submersible", used without qualification, means a vessel as described above of less than 50 tons dry weight.

B. History of Submarine Power Systems

Although divers and diving bells are evident in preclassical history, the first known navigable submersible was constructed in 1624 by Cornelius Van Drebbel, a Dutch physician. Van Drebbel's boat was powered by oars extended

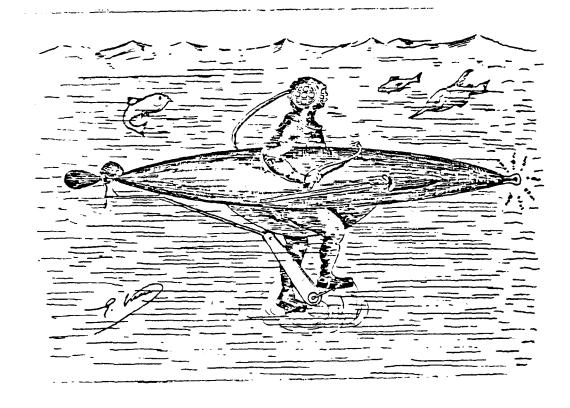


FIGURE 1.1

AQUAPEDE, A Man-Powered Submersible by Alvery Templo (2)

through greased-leather seals in its wooden hull, and although the vessel's dimensions are not known, she was capable of carrying twelve people surviving on the "quint-essence of air". (1)

Manpower continued to provide propulsion for submarines up to the American Civil War. David Bushnell's one-man Turtle which saw action in the Revolutionary War, Robert Fulton's Nautilus built in 1801 for Napoleon, and the Confederate Navy's David which sunk a Union warship in Charleston Harbor were all powered by hand-cranked screw propellers. (2) Fulton's submarine also featured a single foldable mast and sail for surface propulsion. (1)

After 1860 there was increasing interest in submarine boats in both Europe and the U.S., and several innovative methods were used for propulsion. In 1863, Frenchmen Brun and Bourgois launched a 136 ft. long submarine, the <u>Plongeur</u>. <u>Plongeur</u> was propelled by a compressed air motor driving a screw propeller. Compressed air was stored in a single large tank and was also used for buoyancy tank service. (1)

Steam propulsion, both on the surface and submerged, was used in four submarines built by Nordenfeldt and Garrett in England in the 1880's. The Nordenfelt, No. 4, described by Spear (1) was 125 ft. long and had a submerged displacement of 245 tons. With 150 psi steam, her power plant could develop 1,000 horsepower for a surface speed of 15 knots. Submerged, steam was drawn from superheated water in the boiler itself

and in special steam storage tanks to provide an expected submerged speed of 5 knots for four hours.

In the late 1880's, the gasoline engine, steam, and storage batteries were all used for submarine power. The 30 ton French submarine Gymnote, launched in 1888, used a storage battery and a 55 HP motor driving a single screw. The Narval, also built in France, was launched in 1889 and was the first submarine which used a power system both for surface propulsion and for recharging batteries used in submerged service. The Narval had a submerged displacement of 200 tons and used a petroleum fired water-tube boiler for steaming a 250 HP triple expansion engine. The details of Narval's electric plant are not known, although she was said to have a 70 mile submerged range at 5 knots. (1) The American submarine designer, Simon Lake, was the first to use an internal combustion engine for submarine power. His Argonaut First, launched in 1889 and designed for salvage, was powered by a 30 HP gasoline engine that was snorkled to the surface with two hollow masts for intake and exhaust. (3) The Argonaut also featured powered wheels as well as a propeller for bottom propulsion and a diver's compartment with an airlock. (1)

The real breakthrough in military submarine propulsion was the combination of the internal combustion engine with the lead-acid storage battery. John Holland's SS-1, delivered to the U.S. Navy in 1900, incorporated many of the features developed over the previous two decades of submarine activity.

Named the <u>U.S.S. Holland</u>, she included many innovations that were not fully appreciated until the 1950's - a hull form optimizing submerged performance, minimum reserve buoyancy, a small streamlined superstructure, and a large diameter, slow-turning propeller mounted on the longitudinal axis of the hull. The 75 ton <u>Holland</u> was powered by a 50 HP gasoline engine on the surface and a 50 HP motor submerged. Her electrical power was furnished by a 60 cell lead-acid battery with a capacity of 1,500 amps at a four hour discharge rate. (1)

Although the gasoline engine was soon replaced by the much safer diesel and specific energy of lead-acid batteries improved considerably, all military submarines through World War II had, in principle, the same type power plant as Holland. In the 1940's several attempts were made to overcome the submerged speed and endurance limitations of battery power. England, Germany, and the U.S. developed experimental boats using hydrogen peroxide and diesel oil to run steam turbines. These plants provided high power, but were considered unsuccessful for their high cost, very high oxidant consumption, and questionable safety. (4,5)

Closed cycle diesel engine systems using injected oxygen mixed with recirculated CO₂ were also developed in the U.S. and Germany but were never generally adopted. (6) The first real alternative to diesel-electric power for submarines was the pressurized water nuclear reactor introduced on the U.S.S. Nautilus (SSN-571) in 1955. Presently, all combatant

military submarines are diesel-electric or nuclear powered.

C. The Manned Submersible - History and Current Trends

The combatant military submarine has always operated at relatively shallow depths. In fact, until 1934, the record for deep submergence was held not be a vessel, but by salvage divers who had reached a maximum depth of 190 m., but in that year, Professor William Beebe took a 2 1/2 ton spherical steel bathysphere to the unprecidented depth of 923 meters. Beebe's bathysphere, built by Otis Barton, was negatively buoyant and supported from a surface vessel by a steel cable. Electrical power was provided from the surface through a 1,000 m. long cable several feet of which, on early dives were forced through the stuffing tube into the sphere by water pressure.

The first modern submersible which meets the definition of this study was designed and built by the Swiss physicist, Auguste Piccard. In 1939, Piccard began construction of the FNRS-2, a bathyscaph or "deep boat". Construction was interrupted by World War II and the FNRS-2 was not tested until 1948. Designed for depths of 4,000 m., the FNRS-2 was powered by an externally mounted, pressure-compensated leadacid battery of 14 cells and 900 amp-hrs which ran two 1 HP motors, lights, and life-support equipment. A reserve battery was also carried external to the pressure sphere. The FNRS-2 had only limited horizontal maneuverability with a speed of about .2 knots.

From 1939 to 1960, the history of submersibles was written almost entirely by Piccard. The FNRS-2 was modified by the French Navy, redesignated the FNRS-3, and operated extensively in the Mediterranean in the 1950's. In 1953, Piccard launched the bathyscaph Trieste which eventually, in January of 1960, dove to the deepest known part of the world's oceans, the Challenger Deep at 10,912 m. in the Pacific Ocean. Trieste has undergone several significant modifications and is still maintained in an operational status by the U.S. Navy. Her initial power source was lead-acid batteries mounted in the pressure sphere which drove her two 2 HP motors for a maximum lateral speed of .5 knots. As presently configured, she carries externally mounted, pressure compensated silver-zinc batteries of which 16 cells provide 5,000 amp-hrs. at 24 V. and 80 cells provide 952 amp-hrs. at 120 V. The 120 V. batteries drive three stern-mounted 6.5 HP motors for a speed of 2 knots for 12 hours. (3)

Three factors in the early 1960's were largely responsible for a boom in submersible construction - Piccard's achievements especially <u>Trieste's</u> descent to the bottom of Challenger Deep; an increasing public interest in ocean science; and deep ocean surveillance and salvage efforts subsequent to the loss of the nuclear submarine <u>Thresher</u> at 2560 m. in the North Atlantic.

Between 1960 and 1968, more than 50 submersibles of significant capability were constructed. Large corporations such as General Dynamics, General Mills, Reynolds Aluminum, and

Lockheed invested heavily in submersible programs. By 1968, however, the economic realities of submersible operation had become apparent. This and the realization that government funded "space programs" for ocean exploration were not going to materialize led to the abandonment of many submersibles under construction and to the lay-up or sale of almost new vessels. All of the large U.S. companies, except Lockheed, abandoned self-financed submersible construction, and the field was left to a few small companies specializing in submersibles and diver support equipment.

Since 1963, submersible construction and operation has stabilized, and the pattern established since then seems likely to continue barring some strong new impetus for deep ocean exploration. Presently, governments and a few non-profit research organizations maintain a small fleet of very capable submersibles for salvage, surveying, submarine rescue, and the installation and maintenance of underwater military and oceanographic equipment. The U.S. Navy has a strong overall submergence capacility with the submersibles Sea Cliff, Turtle, Trieste, and the nuclear-powered NR-1 presently operational. (7)
In the seventies, the U.S. Navy also acquired two "Deep Submergence Rescue Vehicles" (DSRV I & II) designed solely for rescuing the crews of disabled nuclear submarines.

Commercial activity in the seventies has been dictated almost completely by the needs of the offshore oil industry.

New oil field activity, primarily in the North Sea, has led to

the continuing construction of a fleet of small but versatile submersibles to build and service offshore drilling rigs and pipelines. In 1976, for instance, there was a 30% increase in available undersea vehicles primarily to support petroleum activities, (7) and if present trends in oil exploration - the move to deeper depths and more extreme ocean environments - continue, an increase in commercial manned submersible activity will likely continue also. Generally, the point where submersibles become competitive with divers is a function of depth, but this depth is much shallower in North Atlantic currents and cold—than in the Gulf of Mexico. One company in the North Sea believes that this economic cross-over is as shallow as 120 m., and submersible activity there reflects this with three companies operating 12 submersibles in 1977. (8)

Unlike the 1960's, submersibles today are carefully designed to meet very specific mission objectives. Commercial submersibles will become more depth-capable, more powerful, and more versatile in the future, but this evolution will occur slowly and only when definite needs and economic viability are demonstrated.

D. Present Submersible Power Systems

Submersible power systems today are dominated almost completely by the secondary storage battery and more exactly by the pressure-compensated lead-acid battery. Busby's (3) survey of electric power sources in 97 manned submersibles

reveals the following breakdown: 86 use lead-acid batteries; 6 silver-zinc batteries; 2 nickel-cadmium batteries; 2 surface power; and 1 (the NR-1) a nuclear reactor. In 1978, an oxygen-hydrogen fuel cell power plant was installed on Lockheed's Deep Quest, and is presently being evaluated. A summary of basic power source characteristics for representative submersibles now active is contained in Table 1.1. The characteristics of different power sources will be discussed in succeeding chapters.

TABLE 1.1

POWER SYSTEMS IN ACTIVE SUBMERSIBLES

	(TONS)	DEFINE DEFIN	27.15 5.12.12	SUPPORT (MAN-HRS)	PONER SOURCE(1)	HANER SOUNCE EXCATOR(2)	D.C. VOLTAGE OUTPUT	TOTAL EHENGY KM-HKS (3)	BUILDER	उन
	. s.	1,500	€,	672	2-5	P.C.	112,28	211	Lockheed	-
	٦.	1,950	•	100	L-A	F.C.	30,60	\$	General Dynamics	\$.5
	٠.	3,600	~	917	[- A	F.C.	30,60	40.5	Ceneral Milla	9,6
	٠,	6,000	-	~	2-5	P.C.	24,120	165	Piccard	-
E1	(mma) 00)	;	1	30 days	¥	. H.	:	i	General Dynamics	2
COMPACIAL OR FURLIGIT COVT										
Places 1 2.2	~	1,500	7	100	L-A	P .C.		9	Inter. Hydrodynamics Ltd.	3,9
/15ccs 2, 3 10.7	۲.	2-120 3-900	~	100	L-A	₽.C.		o .	Inter. Hydrodynamics Ltd.	9.6
P15Ces 4, 5, 6 10.9	6.	2,000	~	2	1. →	F.C.		0,0	Inter. Hydrodynamics Ltd.	3.9
Aquarius 1, 2, 3 5.0	•	110	~	108	r-A	ж. Ж.	120	13	Inter. Hydrolynamics Ltd.	9.6
PC-5 C 5.1	۲.	360	~	180	- -₽	и. Н	12,120	91	Petry Sulmerine	3,9
6.5	٠.	750	7	3	L-A	и. Ж.	24,120	22	Perry Sulmarine	9,8
Sekton (1 Vessels) 2.0	0.	900	~	9	L-A	K.H	24,48	4.5	нестом	3,9
Johnson Seallink (2 Vessels) 9.4	•	300	-	22	L-A	m E	Ξ	22	ALCOA	3,9
Ikup Quest 51.4	₹.	2,400	•	204	7	P.C.	28,120	2.10	Lockheed	9,6
Scep Quest 51.4	•	3,400	•	204	F-C	Т.	28,120	700	Lockheed	3,9
X35 23.7	.,	115			r-y	P. C.	120	120	Inter, Hydrodynamics Ltd.	=

⁽¹⁾ S-2 silver-zinc; L-A lead-acid; F-C fuel cell.

(2) P.C. pressure-cuspensated; E.M. encapulated; P.H. in main pressure hull.

(3) Excluding emergency prover.

(4) Carries 24 in ruscue uphere.

CHAPTER II DESIGN OF SUBMERSIBLE POWER SYSTEMS

A. Introduction

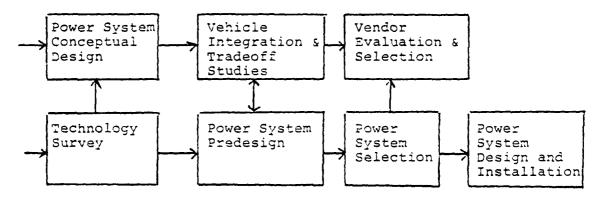
Because both human life and great expense are at risk in any manned submersible operation, the selection and design of a power system must be a well-defined and carefully executed process. Once the mission objectives and the basic characteristics of the submersible are defined, the design elements and constraints applicable to the power system must be established, their implications understood, and the relationships between them defined. With these design elements in mind, feasible alternative power systems should be identified and evaluated in terms of both past submersible practice and present technology. Finally, because of the delicate interaction between various systems, the identified power systems should be compared in preliminary power system-vehicle configurations, and selection made in a systematic trade-off with well-defined criteria.

The power system consists of several components including propulsion and auxiliary motors, lighting, emergency power supply, instrumentation, and the distribution and control sub-systems; however, the main power source has by far the most impact on overall vehicle design. Generally, the energy storage and conversion sub-system comprises 75-90% of the total weight and volume of present submersible power systems. (3)

Although the general type and size of other components must be considered, the power source itself will receive most of the attention in early design and selection processes.

Finally, the design of the power system must be fully integrated into the total vehicle design process. Manned Submersibles (3) by Frank Busby covers all aspects of submersible design, and a proposed flow of events in power system design from reference (12) is shown in Figure 2.1. This chapter will review the important elements involved in submersible power plant design, examine the selection process, and survey alternative power sources.

FIGURE 2.1
POWER SYSTEM SELECTION PROCESS (12)



B. Design Elements

Major factors that must be considered in the design of submersible power systems are:

- Operating depth
- Power source location and protection
- Power source volume and weight

.... Vehicle speed and propulsive power requirements

.... Auxiliary power requirements

.... Endurance

.... Replenishment of power

.... Distribution and Control

.... Reliability and Maintainability

.... Integration with other ships systems

.... Material compatability with sea water

.... Safety

.... Cost

1. Operating Depth. This is perhaps the most single important environmental consideration in all aspects of submersible design, and it imposes many constraints on the power plant. Pressure in the deep ocean can be approximated by ignoring atmospheric pressure and assuming linear variation in the density of sea water with depth as:

$$P = .444d + .3 \left(\frac{d}{1,000}\right)^2$$
 psi [1]

where d is the depth in feet. Thus, even a moderate operating depth of say 1,500 ft. requires that pressure vessels must be designed to resist more than 45 atmospheres.

Designing structures to resist extreme pressures results in internal space that is both small and difficult to arrange. Although stiffened cylinders are sometimes used at shallower depths, a sphere is the most efficient shape, in terms of its weight to displacement (W/Δ) ratio, for resisting external pressures. All active submersibles with a depth capability exceeding 2,500 ft.

use a sphere as the main pressure structure. (3)

Pressure is one of many factors which dictate small size for submersibles. The collapse pressure of a hollow sphere is proportional to the square of its shell thickness to radius ratio (h^2/R^2) . An extreme example is the <u>Trieste II</u>. Designed for 20,000 ft., she has a high-strength (HY-100) steel pressure sphere which is 84 in. in diameter and from 4 to 6 in. thick. (3)

- 2. Power Source Location and Protection. There are three basic choices for power source containment:
 - a. Main Pressure Hull. As mentioned above, the pressure hull is usually a small cylinder or sphere, and internal arrangement space is limited. Locating the power source here will either decrease the payload and internal volume available, or it will increase the size and weight of the hull. Systems using caustic electrolytes or inflammable fluids may cause increased safety problems located in the personnel sphere. Advantages in this system include easy adaptability of surface designed batteries, ease of maintenance, simple circuit design, and maximum protection from sea water. Although some commercial submersibles with limited depth capability locate their main power sources in the personnel sphere, more advanced systems usually use this scheme only for emergency batteries.

b. External Pressure Capsules. Many small commercial submersibles use this method of containment for battery systems, (3) and it is the method chosen for the alkaline fuel cell system developed by United Technologies for the DSRV and presently installed on Deep Quest. (15) External containment frees space in the main structure and isolates dangerous liquid or gas from the personnel sphere. Often external battery pods are droppable to provide emergency buoyancy. The disadvantages of this system are increased total weight, the necessity of engineering separate pressure structures, and increased drag if capsules are mounted external to the main fairing. c. Pressure Compensating Systems. Of the three, this method of containment is the one used in most modern submersibles, (3) and its one advantage ~ minimum total weight - is important enough in submersible design to overcome many problems experienced in actual operation. Disadvantages associated with pressure compensation include difficulties in maintenance, salt-water contamination, and problems associated with gassing. A complete discussion of battery compensating system configurations and problems is available in Reference (16). In general, battery cells are surrounded by oil which provides insulation and pressure compensation. Provisions

must be made for pressure relief, for draining the system, and for preventing evolving gases from carrying electrotye out of the battery. The latter problem has been encountered in lead-acid systems, and was the cause of early grounding problems in the DSRV Ag-Zn system. (17)

Fuel cell and heat cycle systems which use liquid fuels and/or oxidents may also use pressure compensated or hybrid containment systems. The Asthom hydrazine-hydrogen peroxide fuel cell system maintains both reactants and cell at ambient sea pressure. (19) Proposed heat cycle systems would use encapsulation for the energy converter and pressure compensated tanks for fuel. Oxidant might be carried as compressed oxygen or hydrogen peroxide liquid. (6) Liquid reactants, if available for an efficient, light-weight energy system, could provide near neutral buoyancy in a pressure compensated arrangement.

3. Weight and Volume. In general a submersible power system should be as light and a nearly neutrally buoyant as possible. Excluding bathyscaphs and exceptional vessels like the NR-1, manned submersibles tend to be small. Seventy active submersibles listed in Reference (7) average about 6 m. in length and approximately 9,000 kg. in dry weight. Besides pressure mentioned above,

there are several reasons for this. A small, light submersible will be less expensive, easier to handle and transport, more capable of close-in work, easier to maneuver, and subject to less hydrodynamic drag. In some larger submersibles like the DSRV and the commercial NGS, maximum dimensions are limited by air cargo holds, and most submersibles must be easily launched and recovered at sea. Sinclair (19) estimates that only 30-40% of the capital investment of a system is in the submarine itself. Increasing size not only costs more directly, but requires larger and more complicated support ships and handling equipment.

Depth capability provides strong impetus for keeping power systems light. In a complete submersible, the sum of all weights must equal the weight of seawater displaced by all volumes (see Appendix 1). Because of the thickness of hull required, the buoyancy provided by the pressure sphere is rarely enough to support the whole vessel, and in very deep diving submersibles, the pressure sphere itself is negatively buoyant. The syntactic foam usually used as positive ballast is expensive, and major systems external to the pressure hull, such as the power source, should provide minimum possible negative buoyancy.

4. Energy Requirements. It is difficult to generalize about the total amount of energy required for submersibles. Table 2.1 summarizes predicted requirements for different

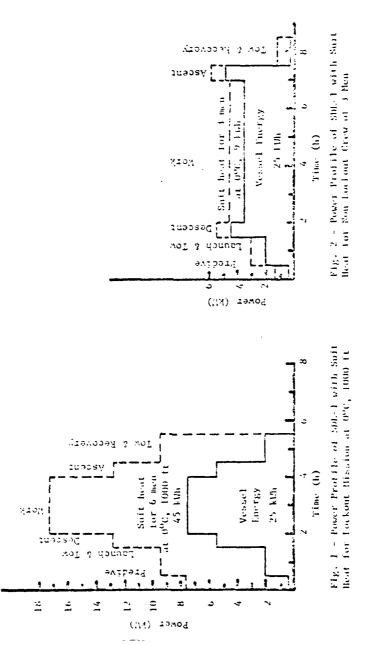


FIGURE 2.2 POWER SPECTRUMS FOR A 14-TON SUBMERSIBLE

missions from Reference (15), but actual needs can vary widely from these ranges depending on the vessels size, the actual tasks performed, and ocean conditions.

TABLE 2.1
POWER REQUIREMENTS (15)

Winsian		(KW)	Maximum
Mission	Ave.	Max.	Duration (hrs)
Ocean survey/mapping	20	40	12
Salvage/recovery	30	60	8
Rescue	20	40	2
Search	10	40	12

The best procedure for sizing energy systems is that recommended by Busby (3) and followed in References (20) and (21). Once power requirements for the various ships systems are known, a power spectrum against time can be constructed for expected missions and emergency conditions. Figure 2.2 shows projected power spectrums for a 15 ton Canadian submersible with diver lock-out and suit heating requirements. The most carefully constructed power spectrum, however, cannot predict exact operating circumstances, and power system designs are assigned margins as high as 25-50%.

a. Propulsion Power. Propulsion is usually the major power load. The power required to drive a submersible underwater is given by:

$$P = K_d V^3$$
 [2]

where K_{d} is a constant depending on water density,

surface area, and drag coefficient, and V is velocity relative to the water. Formula 2 reveals the great cost, in terms of power, of increasing submersible speed or of operating against strong currents.

Propulsion systems are covered extensively by Busby. (3) With few exceptions, submersibles use electric motors to drive screw propellers either directly or hydraulically. Generally, the weight and volume of electric motors and drive systems is small compared to the energy storage system, and Lund and McCartney (22) recommend maximizing motor efficiency at the expense of size in order to lower total energy requirements.

b. Other Loads. After propulsion, external lighting and manipulators or other work systems are generally the greatest consumers of energy. The Deep Quest, a large and highly capable submersible, carries a total of 9 KW in lighting, while even a modest vessel like the Pisces 1 has two 1,000 watt external lamps. (9) Power for manipulators and other external tools is, of course, highly dependent on specific tasks. Suit heating for the lock-out submersible planned in Reference (21) would require 10 KW, half of the total installed power, and a modest underwater welding capability would require as much as

16 KW. (4)

Besides the variable loads of propulsion, lighting, manipulators, and other work equipment, the power system must maintain a relatively constant load for life-support equipment, navigation aides such as gyrocompass and sonar, communications equipment, and monitoring instruments. For a typical submersible, these "hotel" loads total on the order of 1 kW. (3)

5. Endurance and Replenishment of Energy Systems.

Habitability conditions aboard most submersibles limit single dive time to around 8-10 hrs. (3) while endurance of power-systems is highly dependent on the specific mission. A typical commercial submersible on a task requiring little propulsion might go through two or three crew changes before battery recharge, while a high speed (2-3 knot) operation would be limited to one or two hours. Ideally, the power system should be designed so that in any mission it is not the limiting factor.

Failing that, the goal would be as much energy as possible within the design constraints.

Replenishment of present systems is generally accomplished by recharging batteries after the submersible is secured aboard its support vessel. Charging time is on the order of 3-12 hrs. (9) The design ideal in this case would be power replenishment in the same order

of time as crew replacement. A new commercial submersible, the NGS, features compensated lead-acid battery packs which can be quickly interchanged, (11) and the gaseous hydrogen and oxygen for Deep Quest's fuel cell system can be replenished in less than one hour. (15) In advance systems which require liquid or gas energy storage or use unfamiliar technology, the design effort must deal fully with replenishment arrangements.

6. Power Distribution. Few generalizations can be made about power distribution systems. Some submersibles use only d.c. power at one voltage level while others require several different voltage levels of both d.c. and a.c. power. The general power distribution system for Sea Cliff is illustrated in Chapter IV and general guidelines for distribution systems design can be found in Busby. (3)

Items of primary concern in power distribution systems are:

- a. Redundancy and reliability in the primary system.
- b. Protected emergency power for vital systems.
- c. The design of hull penitrators and electrical connectors. (An area of vital concern and much innovation in submersible design, this is addressed in detail in References 9 and 23.)
- d. Cable, junction boxes, and distributor panels that are watertight, encapsulated, or pressure compensated.
- e. System design to limit electrical interference with electronic instruments. (A serious problem

in past designs, this is treated extensively in Reference 9).

7. Other Factors. The implications of other design elements are more self-explanatory or depend strongly on exact requirements of the individual design.

Acquisition and operating costs, reliability, and maintainability are important considerations in any submersible design. Closely related to cost and maintenance would be factors such as the developmental risk in new systems, commonality with other systems, and the availability of operators trained in particular power plants.

As in any system designed for ocean operations, materials must be examined with respect to their corrosion resistance in sea water, their compatability with fuel, exident, and, or electrolyte in the power system, and their galvanic behavior with other vehicle materials. Because submersibles must operate in seas during launching and recovery and are subject to accident, the power system should have a specified degree of physical durability and shock resistance.

Submersible operations are inherently dangerous, both when submerged and during surface handling, and human safety must be a primary concern in any power system design.

- 3. Summary. From the above discussion, some of the desirable attributes of power systems for small submersibles are as follows:
 - a. Maximum power density.
 - b. External encapsulated or pressure compensated system with minimum possible weight/displacement ratio.
 - c. Size and configuration easy to arrange within the streamlined external fairing.
 - d. Sufficient power to meet required loads and transients.
 - e. Sufficient energy to meet all mission profiles with reserve for emergencies.
 - f. Replenishment of power in smallest possible time. (Ideally, same order of time as crew replacement.)
 - g. Distribution system with high redundancy, minimum hull penitrations, and minimum electrical interference.
 - h. Separate emergency power system in the personal sphere to operate life-support and other vital equipment.
 - i. Minimum acquisition and operating costs consistent with design requirements.
 - j. Maximum possible reliability, availability, and maintainability.
 - k. High degree of personal safety in both operation and support.

C. <u>Selection Process for a Power System</u>

Rich $^{(12)}$ suggests that a systematic selection methodology should be applied to submersible power systems. This procedure, developed largely in aerospace applications,

requires identification of the important selection criteria such as the "design elements" listed above, the assignment of numerical values (weighting factors) to the relative importance of each criteria, and the grading of each alternative system. Grading is on an arbitrary scale (say from 1-10) depending on how well a system meets a given specification. For each alternative the product of weighting factors and grades are summed producing a numerical "figure-of-merit". Although it is somewhat artificial, and heavily dependent on the evaluaters judgement, such a procedure can be an important design tool. It forces evaluation of a given system against all the important factors in a design, illustrates the various weak and strong points of competing schemes, and provides a record of the selection process.

The actual selection will, in almost all cases, depend on economic considerations. Available systems which meet design requirements will be compared as to their acquisition and operating costs, or the requirements will be relaxed to fit an affordable system.

D. Alternative Energy Sources

Alternative methods of primary energy conversion are shown in Figure 2.3. Generally, the electrochemical systems - fuel cells and storage batteries - have much higher conversion efficiencies than alternative methods. Electrochemical systems avoid the use of heat which always entails an

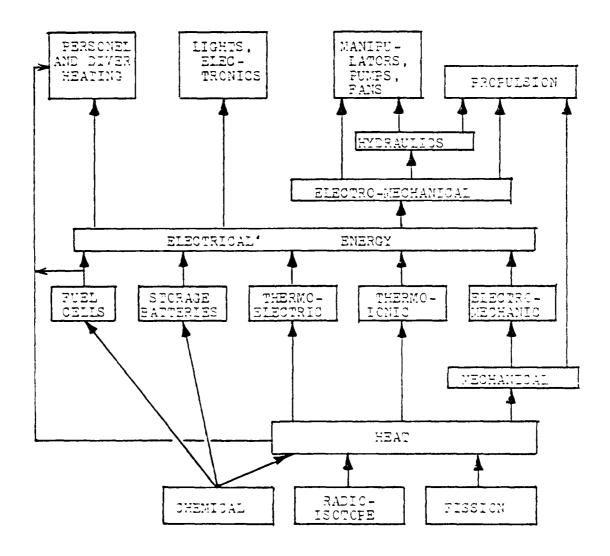


FIGURE 2.3
EMERGY CONVERSION ALTERNATIVES FOR SUBMERSIBLES

important increase in entropy, and they avoid the inefficiencies associated with engines, boilers, and turbines.

For conversion into electrical energy, the watt-hr. (whr) efficiency of lead-acid storage batteries at normal discharge rates is between 75% and 80%, while efficiencies for H₂-O₂ fuel cells are theoretically as high as 90% and for existing systems range between 50% and 75%. (Fuel cell efficiencies are discussed further in Chapter III.) In comparison, values ascribed to thermal engines are much lower. Estimated efficiencies for alternative closed-cycle combustion systems are as follows: Diesel 23%; Wankel 18%; Stirling 35%; and Brayton 32%. (21) Conventional thermal engines have much higher efficiencies (Diesels range from about 30-45%) than these specialized systems, but still lag well behind electrochemical systems. Present thermoionic and thermoelectric generators operate at less than 10% efficiency. (22)

Many other characteristics besides efficiency must be examined in selecting an energy system. Present batteries have comparatively low energy density, while available fuel cell systems are relatively expensive. However, the high efficiency of electrochemical systems makes them competitive in the long run for any portable energy system.

Currently, only three basic sources of energy have been used in small submersibles - secondary storage batteries, fuel cells, and surface power. Fuel cells will be discussed in detail in Chapter III. Here the basic characteristics of

other possible systems will be reviewed.

1. Batteries. As mentioned in Chapter I, electrochemical storage batteries have a long history in submarine applications, and are presently the overwhelming choice for manned submersible power systems. Because of their relative simplicity, reliability, and low cost, and due to progress in high performance systems, batteries are likely to be used in the majority of submersible systems in the forse able future.

Existing batteries, however, still suffer from the deficiency mentioned by L. Y. Spear in 1901. $^{(1)}$

"The storage battery [is] admirable in some respects, but exceedingly inadequate in others. The principle objection being the well known one of excessive weight and space in proportion to the power developed."

Despite a nearly five-fold increase in specific energy in today's lead-acid battery systems over those Spear was talking about, this critism is still applicable, and many present and projected submersible missions are power limited with existing batteries.

Present systems are lead-acid, silver-zinc (Ag-Zn), and nickel-cadnium (Ni-Cd) secondary batteries, and many different advanced systems have been investigated for submersible use. (22,24,25) The basic characteristics of some systems configured for submersible operations are listed in Table 2.2 reproduced from Reference 24, and a comparison of specific energy and energy density of

TABLE 2.2

COMPARISON OF STATE OF THE ART BATTERY SYSTEM CHARACTERISTICS

	Bank	Banc Call Characterities	t seture	1	21 0 07 A	Mattery for G to Fleed fr Dapen.		3	Of set year	Battery for 10 Dut ft Capith		3	Hery for 20	Bettery for 20 0ud ty tra, di-		
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Max week as also erry (P)	5	110	۲,	2	:	3	3	=	=	2	77	=	;	4 4 /8	3	Low rate
Alapine (F)	8	3	4	2		****	3		;	3,	*	-	:	7/6.7	ž .	Lune or Mediucia
Maynessum (P)	777	3	4 2	:	:	75/2	8	* 01	:	786	ž	£	=	1,212	3	Hydrogen
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present and advanced systems from Reference (22) are shown in Figures 2.4A and 2.4B. Only a few of the most promising advanced systems will be discussed here.

a. Lead-Acid Batteries. Lead-acid batteries are the standard for manned submersibles for many good reasons. They are well proven, inexpensive, rugged, reliable, and easy to service. They have a relatively high cell voltage (2.0 V.), a long life cycle (approximately 300 discharge cycles), and are commercially available in units designed for pressure-compensation. Their major disadvantages are, again, low energy density and problems associated with electrolyte spillage or leakage. Present submersible systems are capable of about 26 whr/Kg at a 6 hr. discharge rate. (22)

Advanced lead-acid systems are capable of 40-60 whr/Kg at the expense of greatly reduced cyclelife, (24) and the Department of Energy is sponsoring development of lead-acid systems for electric vehicles with a goal of 40 whr/Kg. (22) Fairly recently, lead-acid batteries with paste electrolyte have become available. (26) Although they have about the same energy density as present submersible systems, these batteries are not subject to leakage due to battery orientation.

b. Silver-Zinc Batteries. At approximately

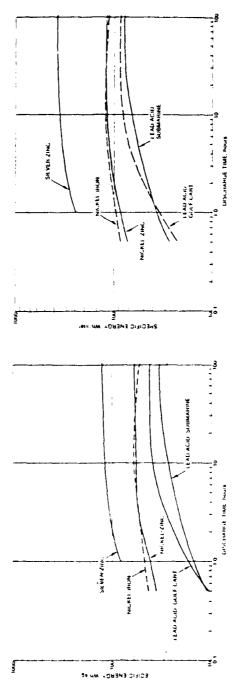


FIGURE 2.4A

Fig. 1 - Specific energy of presently available secondary batterles

Fig. 2 - Energy density of presently available secondary batteries



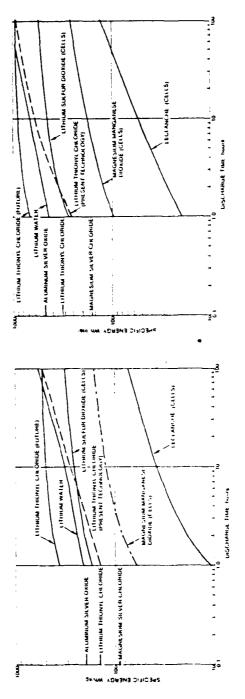


FIg. 5 - Specific energy of advanced primary batteries

Fig. 6 - Energy density of advanced primary batteries

110 whr/Mg, Ag-Zn batteries have four to five times the energy density of present lead-acid systems. They are used as primary power in a few advanced submersibles and provide emergency power on several vehicles. Other advantages of Ag-Zn batteries are good tolerance to high discharge rates and long dry storage life. On the other hand, Ag-Zn have several serious deficiencies. They are expensive, have a short life (10-20 cycles) for deep discharge, and have a wet storage life of 2-18 months. (24)

In the past Ag-Zn systems have also had reliability problems. A survey of Ag-Zn installations in seven different vehicles shows two failure modes: internal shorts and a gradual loss of capacity with cycling which is not generally predictable. (27)

The DSRV Ag-Zn system, requiring multi-drive, rapid turnaround missions, was plagued with grounding and early loss of capacity. The grounding problems were eventually traced to RCH electrolyte being forced onto the tops of cells by gassing and were corrected with new battery caps, but there is still no reliable method for determining the state of charge of Ag-Zn batteries. With improvements, the DSRV battery system is limited to about 9 cycles before replacement. (17)

c. Nickel-Cadmium. Ni-Cd batteries are presently

used in two manned submersibles. (3) Although they have a slightly higher energy density and a comparable cycle life, they are more than twice as expensive as lead-acid batteries and have a low cell voltage (1.0-1.3 V).

In the past, Ni-Cd batteries were desirable because they were available as completely sealed cells. With the development of sealed, paste-electrolyte lead-acid batteries, it is doubtful that Ni-Cd batteries will be competitive as major power sources for submersibles.

- d. Advanced Secondary Batteries. There are many secondary battery systems now under development which could be used in future undersea applications. The predicted characteristics of likely systems are shown in Table 2.2 and Figure 2.3. The most promising among these still require significant research, and they have operating characteristics which could be major problems on small submersibles. The lithium-metal sulfide batteries, for example, may be capable of 155 whr/Kg for as much as 1,000 cycles, but they must operate above 400°C. with a molten salt electrolyte. (22)
- e. Advanced Primary Batteries. Two primary

 (un-rechargeable) battery systems appear to have

 significant potential for submersible applications.

The lithium-thionyl chloride battery has extremely high energy density (500-600 whr/Kg), a cell voltage of 3.6 V, long operating life, good low temperature performance, good voltage regulation and can be pressure-equalized for submergence. (25) Early batteries would explode if short circuited or if exposed to high temperatures, but these problems have been corrected in recent versions. (22) Other problems have been short shelf-life and sensitivity to cell orientation. Although it is a primary cell, the lithium-thioynl chloride battery is reported to be economically competitive with Ag-Zn secondary systems. (24)

Another promising primary system is the lithium-water battery. In this system, a consumable lithium (or lithium alloy) anode is coupled with iron or nickel cathode structures. Seawater electrolyte is circulated through the cell, and the power level is adjusted by controlling the electrolyte composition. (25) Several refinements to the basic cell have been made, and a 25 kw lithium-water-hydrogen peroxide battery under development is expected to yield 440 whr/kg at a 30 hr. rate. (22)

2. Other Power Sources

a. Dynamic Converters. A number of dynamic machines have been proposed for submersible power

sources. These include open and closed cycle combustion engines, closed cycle engines using heat storage or radioiostope energy, and mechanical energy storage systems.

1. Combustion Engines. Among candidates in this class are piston, Wankel, Stirling, and Brayton engines. Advantages are high specific power and high power density. Open cycle combustion systems require overboard elimination of exhaust products resulting in increased fuel consumption with depth and a constantly changing ballast condition. Closed cycle systems require onboard treatment and stowage of combustion products. In this respect, hydrogen fuel (although storage efficiency is poor) is attractive because it requires less oxygen for combustion than hydrocarbon fuels and because the product water is relatively easy to handle. (21) General disadvantages of combustion engines compared to electrochemical systems are noise and vibration and relatively high specific fuel consumption. Combustion systems might be desirable for missions with high power, but low total energy requirements. (6)

A recent Canadian Government study found that a 10 kw closed Stirling system with waste heat provisions for dive heating was the preferred option among engine systems for their 14 ton sub-

- mersible. (21) Aeroject-General has developed a closed cycle diesel system in two packages (60 and 1,000 kwh) which completely encapsulate the energy system. The 1,000 kwh module is 4 ft. in diameter, 20 ft. long, and at 16,000 lbs., has approximately the same energy density as the Ag-Zn battery. (3)
- 2. Closed Cycle Engines Without Combustion.

 Several schemes have been proposed for using engine systems with thermal energy storage or radioiostope heat sources. The Stirling engine is often mentioned for these applications due to its high thermal efficiency.

Thermal energy storage in the form of sensible heat storage combined with a closed cycle engine could result in a relatively simple system with a high cycle life. It has been estimated that lithium hydride could provide energy storage up to .14 Kwhr/Kg not considering conversion equipment, (14) and sensible heat storage has been demonstrated with a closed Brayton cycle engine. (22) Problems exist in the stowage of hot materials with high sensible heat and, in the case of hydrides, with material embrittlement. According to Lund and McCartney, (22) this scheme is best suited to missions where high weight and volume are acceptable trade-offs for simple operation. Thermal storage systems using

phase change in inorganic salts are also conceivable, although not practically developed.

Some studies (12,13,14) have suggested radioisotope heat sources for closed cycle power converters; however, high costs, low power density, high total weight with required shielding, and biological hazards make them unlikely candidates for manned submersibles.

- 3. Mechanical Energy Storage. Generally, these systems have a high power-to-energy ratio but a specific energy lower than modern storage batteries. (22) Advanced flywheels might have application in a system requiring high short-term power, but this requirement does not apply to submersible systems to nearly the same degree that it does to surface vehicles. Compressed gas energy storage is simple and cheap, but even at high pressures provides about half the specific energy of lead-acid batteries. (22)
- b. Thermoionic and Thermoelectric Generators. The direct conversion of heat to electricity, although promising in terms of system simplicity, does not appear to be a near term possibility for submersibles. Current thermoelectric power converters have efficiencies of less than 10%, and thermoionic

converters require operating temperatures in excess of 1,500°C. (22) Radioiscippe thermoelectric generators are available in small sizes (10) with and appear feasible at higher power levels with convective heat-transfer loops, (12) and thermologic converters with nuclear heat sources have been mentioned as candidates for submersibles in the low power (1-10 km) range, (14) but these systems offer the disadvantages of radioiscippe systems and the low efficiencies of direct conversion.

- water reactor provides power for one of the submersibles fitting the definitions of this study,
 nuclear reactors are unlikely candidates for future
 manned submersibles. The <u>MR-1</u>, at 400 tons displacement, cost approximately 599 Million to design
 and build in 1969. (10) The size, weight, and cost
 of nuclear heat sources, in general, rule them out
 for any applications except those requiring several
 weeks submerged endurance.
- d. Surface Power. Two active manned subrersibles obtain their power from surface vessels. There are many advantages to such a system including high available power levels and easy launch and retrieval. Disadvantages include additional support requirements in the cable, winch, and generator and more

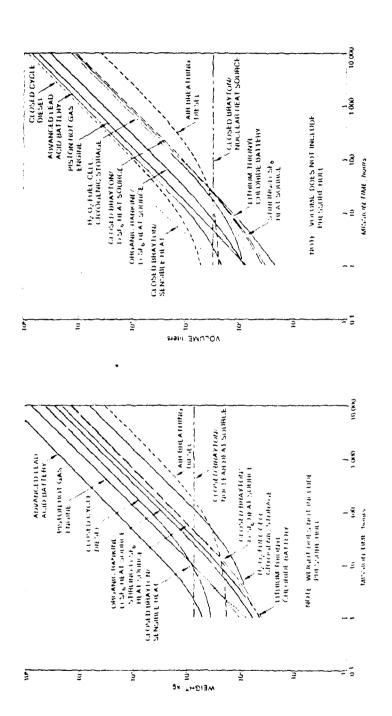
limited maneuverability. Difficulties in engineering the cable and handling system increase with depth, and <u>Suppy</u>, the most capable of the two, has an operational depth of 1,000 ft.

Busby (3) says that from a safety standpoint, the cable offers increased chance of fouling but also provides a good method of emergency retrieval.

2. Comparison of Available Systems. Despite the number of alternatives discussed above, only three basic systems are readily available for submersible installation - secondary storage batteries, United Technology's PC-15 alkaline fuel cell system (discussed in Chapter IV), and surface power. Systems that appear most promising in the near future include other fuel cell systems, primary catteries of the lithlum-thionyl chloride or lithium-water types, and closed cycle Brayton and Stirling entines.

Figure 1.3 simplares estimated weights and volumes of some advanced systems in a 13 km submersible power plant. It must be emphasized that such a comparison is meaningful only in the context of specific requirements. The weight of a pressure compensated battery system will be independent of operating depth while depth may be a major factor contributing to the weight of other systems. A high gower requirement may favor an engine system with high operation fuel consumption while high

FIGURE 2.5 COMPARISONS OF WEIGHTS AND VOLUMES OF ALTERNATIVE 10 KW POWER SYSTEMS (22)



endurance requirements will deman more efficiency. In one case, ⁽²¹⁾ a fuel cell system with lower efficiency than another was counted as a possible advantage because of greater thermal waste for diver heating.

Costs are especially difficult to assess for new systems. Submersibles represent a very limited market, and even well-developed technologies from other applications require extensive alteration and testing for undersea use. Cost comparisons from Reference (21) are presented in Table 2.3. These were based on extensive communications and contract studies with various vendors, but can still only be described as "order-of-magnitude" estimates. Capital costs for those systems using hydrogen and oxygen include \$140,000 for storage tanks which could be highly variable depending on alternative storage methods. The cost per dive figures include amortized costs of development, but do not include fuel costs. (21)

Due to their overall low cost, secondary storage batteries will continue to be the standard power source for submersible power systems. In cases where the weight penalties and limited energy density of present batteries are unacceptable, several advanced systems are realistic candidates for future applications. The electrochemical fuel cell, presently one of the most attractive alternatives, will be examined in the next chapter.

Table 2.3 - Cost Comparison (Nef. 21)

System	Development Cost	Development Risk	Capital	Converter	Cost per <u>Dive</u> (2)(3)
Silver-Zinc Nattery	C	MIL	\$100,000	10 cycles	\$11,000(11,000)
10 kW Wankel	000,008\$	MODERATE	\$200,000	3,000 hrs.	3,000 hrs. \$ 1,000(500)
10 kW Stirling(4)	\$300,000	rom	\$240,000	3,000 hra.	3,000 hrs. \$ 900(500)
20 kW Stirling	\$4,000,000	LOW TO MODERATE	\$300,000	3,000 hrs	3,000 hrs \$ 6,000(1800)
20 kW Alk. Fuel Cell	0	n1 C	\$640,000	5,000 hrs	5,000 hrs \$ 1,200(1200)
10 kW SFE Fael Cell	\$800,000	MODERATE	\$200,000	10,000 hrs	10,000 hrs \$ 1,300(500)
20 kW SPE Fuel Cell	\$1,000,000	MODERATE	\$240,000	10,000 hrs	10,000 nrs \$ 1,600(600)

Includes \$140,000 for fuel and oxidant storage. Assumes 150 dives per year. Unbracketed numbers assume 1 unit produced; bracketed numbers, 5 units. Assumes suitable prototype engine available. 3333

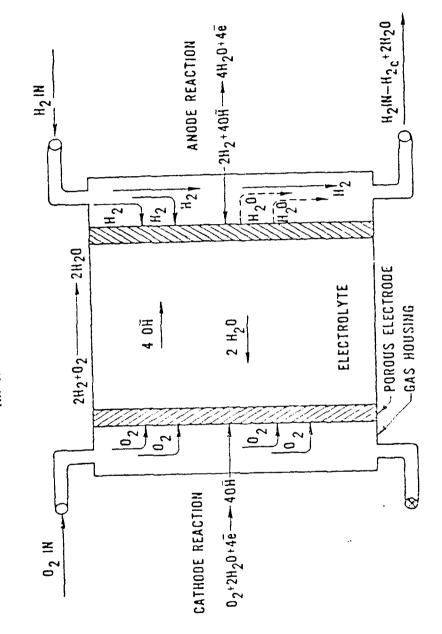
CHAPTER III FUEL CELL POWER FOR MANNED SUBMERSIBLES

Chemical fuel cells have been proposed for submersible power systems since their first successful application to space flight in the early 1960's. With sufficient development many different types of fuel cells might be adaptable to small submarines. The present study, after exploring fuel cells in general, will concentrate on three relatively advanced systems - United Technologies' PC-15 power plant and the Alsthom hydrazine-hydrogen peroxide systems which have been engineered into complete submersible power systems, and the General Electric solid polymer electrolyte cell which appears adaptable to submersible use with little technological risk.

A. The Chemical Fuel Cell.

- 1. Definition. A fuel-cell is an electrolyte cell which is continuously supplied with electrochemical reactants as electrical energy is drawn from the cell. Theoretically, any two chemical species which react electrochemically can be used in a fuel cell. The relatively simple reaction of hydrogen with oxygen has been used most successfully in current applications, and it will demonstrate the basic operation of fuel cells.
- 2. The Basic H_2 - G_2 Fuel Cell. Figure 3.1 illustrates the general reaction process in a hydrogen-oxygen fuel cell with alkaline electrolyte. In this case, hydrogen

FIGURE 3.1 AN ALKALYHE FUEL CELL



gas fuel is fed to the anode where it reacts with hydroxol ions to produce water and electrons:

$$2H_2 + 4 OH \longrightarrow 4H_2O + 4e$$
 [1]

while at the cathode, oxygen combines with water and electrons to replenish hydroxol ions:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$
 [2]

A cell with acid electrolyte operates in an analogous fashion with hydrogen ions "carrying" the reaction and water forming at the cathode (see Figure 3.1):

$$2H_2 - 4H^+ + 4e^-$$
 [3]

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$
 [4]

In both cases, the overall reaction produces water with one Faraday of charge released at the anode for each gram-atom of hydrogen consumed, and the net reaction is:

$$2H_2 + O_2 \longrightarrow 2H_2O$$
 [5]

Even for the simple $\rm H_2-O_2$ cell, the actual reaction mechanisms are much more complicated than indicated above and depend on many factors such as exact electrode materials, electrolyte composition, and the electrical state of the cell. The thermodynamics and kinetics of electrochemical reactions, with specific regard to fuel cells, are discussed in detail in References (28), (29), (30) and (31).

- 3. Efficiency of Fuel Cells. The comparatively high efficiency of electrochemical systems is remarked on in Chapter IV. The isothermal efficiency of the hydrogenoxygen cell in Figure 3.1 is 83.1%, and actual overall efficiencies of operating H_2-O_2 systems range from 503 to 75%. The major losses are due to heat produced by the change in entropy of the reaction system (TAS) and due to irreversibilities in the reaction process. Other inefficiencies occur because of the diffusion of fuel or oxidant across the cell causing direct (vice electrochemical) reactions and due to reactions of other chemicals in the system. The thermodynamic definitions of cell efficiency are reviewed in Appendix 2. For total system efficiency, the power requirements of system auxiliaries such as reactant and electrolyte pumps, heaters, and controls must be considered. In typical systems, these auxiliary requirements will represent 5% or less of total power output. (29)
- 4. Classification of Fuel Cells. Fuel cells can be generally classified by three criteria: reactants, electrolyte, and working temperature. A recent review of fuel cell development by Kordesch (30) shows a great variety of possible fuel cell configurations. In present research, examples range from megawatt level power plants using molten carbonate electrolyte, hydrocarbon fuels, and air to biological cells burning glucose and

oxygen from the blood providing power for artificial hearts. High temperature cells offer greater flexibility in fuel and oxidant usage and reduced catalyst requirements, but are generally in the developmental stage.

- 5. Electrolytes and Electrodes. Given specific reactants and operating conditions, a fuel cell's performance depends on the nature of its electrodes and electrolyte.
 - a. Electrolytes. Typical electrolytes for low temperature cells include aqueous solutions of sulfuric acid, phosphoric acid, or potassium hydroxide. Ion-exchange membranes, such as G.E.'s solid polymer electrolyte, are also used. Cells which operate much above the boiling point of water use very concentrated acid or basic solutions or, above 350°C, molten alkaline carbonates. (29)

Generally, the electrolyte must have high electrical conductivity and high mobility of the ionic species to minimize ohmic and concentration losses across the cell. Ideally, the ion which participates in the reaction should carry all of the current. Conversely, the electrolyte should have negligible electronic conductivity to prevent self-discharging. For low temperature cells, alkaline electrolyte is generally superior to acids because of lower polarization losses at the cathode (29) and

reduced corrosion of electrode and other system metals. However, in systems where carbon dioxide can enter the electrolyte (as a product of hydrocarbon oxidation or as a constituent or impurity in the oxidant), carbonates can form in alkaline systems causing cell degradation. (28) Because of recent advances, solid polymer ion-exchange membranes are a very attractive electrolyte system for low temperature fuel cells. The G.E. solid polymer system will be discussed in detail below.

Depending on reactants and cell construction, reaction products may alter or dilute the electrolyte requiring constant electrolyte treatment, and in all cases provisions must be made for removing heat from the electrolyte system.

b. Electrodes. In order to achieve high specific power, electrodes must provide a large effective area for reaction processes compared to its gross dimensions and weight. Electrodes must also have high electronic conductivity, and should be capable of handling high current densities. Electrode materials should promote the reaction at the highest possible rate, and the specific catalysts used in a fuel cell depend on the nature of the fuel or exidant and in working conditions. In $\rm H_2-\rm C_2$ cells, platinum or platanic alloys generally

catalyse the anode reaction while cathodic catalysts include platanic metals, gold, silver, nickel, carbon, and some intermetallic compounds. (29) The mechanisms of catalytic electrochemical reactions are extremely complex, and in general, only empirical studies accurately predict a specific catalyst's performance.

Because precious metal catalysts are one of the major factors in the high cost of present fuel cells, a great deal of effort has gone into finding alternative electrode materials and into reducing the platinum loading of anodes. (30) Higher temperature systems require lower activity catalysts (reactants at higher thermal energy more easily exceed the activation energy of the reaction), but this must be balanced against the chemical stability of the electrolyte, increased catalyst corrosion and other material degradation, and ease of operation. For low temperature ${\rm H_2-O_2}$ cells as much as \$5% of the cost of precious metal catalysts can be recovered by reprocessing. (15)

6. Fuel Cell Development. The concept of fuel cell energy conversion was proposed by Davy at the beginning of the nineteenth century, and W. R. Grove operated a hydrogen-oxygen cell in 1839. (29) Since then, there have been periods of high interest and experimentation

followed by periods of disenchantment and neglect. In the past twenty years, significant advances have been realized in fuel cell technology, and a great variety of cell types have been proposed and tested. (6) Despite this, relatively few complete fuel cell power systems have actually been built. The 13 systems listed in Table 3.1 probably represent a majority, in total number, of the fuel cell plants with a capacity greater than one KW built in the United States.

The only sustained non-experimental applications for fuel cell power have been in space flight. Since the first Gemini cell was delivered in 1963, fuel cells have provided reliable, lightweight energy systems in many space missions. For the apollo program, United Technologies delivered 90 power plants to NASA, and 16 flights involving a total of 10,750 hours of operation were completed. (15) In general, space power systems are engineered for lightweight, performance, and reliability rather than low cost. Expensive fuel cell systems are competitive because their cost is offset by high energy density which reduces the overall weight to be boosted into space and because power system hardware is a relatively small part of total mission expense.

Many other mobile applications for fuel cells have been tested. These include cars, trucks, motorcycles, tractors, and portable generator sets. For road vehicles

TABLE 3.1 COLPIETE OUGL CELL SYSTEM

Dandacturer	Output	161, 111	Volume	Fig.1 Oxidant	electrolyte	conditions	application	Ref.
Union Carbide	3.7-9.1	1650	800	hydro <u>ren</u> oxygen	Roll Homes	ambient 50-ó0 c.	GM electovan	7
Allis-Chalmers	4.5	540	650	hydrazine air	E	ambient 75-80 c.	US Army portable power	ន
	15		025	<u>भ्रम्भयात्</u>	callode: Ag Koll in asbestos matrix	anbiont 90°C.	Tractor	7
Consanto	09	964		<u>bydrazine</u> air	Kell	95°c.	US Army truck	a
Uni ted Technologies	¢:			hydrogen ozygen	anode: platinised		MASA Apollo	Z
	11-11			hydrouen orygen	screen cathode: Au plated	260°C. 3.75 atm.	MASA Space Shuttle	સ્
	20-30	177(2) 182	182	bydrozen ozygen	KON In asbestos matrix		Submersible OSRV	15
	10	982	Čč0	notural_gas air			PC-11 Utility Fower	21
	1000			Varions hydrogarhone air	VPhospora e acid		Utility Fower (1200hr. test)	5
Alsthom	10	11		Pydrazine perosido	Stainless steel:Co.Au	:	submersible	<u>~</u>
	100	340(2) 300	300	herozine perozide	catalysts Kol	ambrent 70°C.	submersible	<u>~</u>
General Electric		96 6		hydroren ozygen	plat ini sed electrodes	25°¢.	NASA Gemini	33
	-7	Œ		hydrogen ozygen	solid polymer electrolyte	82°c.	NASA	33

⁽¹⁾ Excluding fuel (2) Including containment

fuel cells offer clean, noise-free propulsion; however, present systems do not perform efficiently over the large power ranges required. A promising approach combines high power density advanced batteries for acceleration with fuel cells for sustained low-level power and battery charging. Union Carbide tested a hybrid fuel cell-battery system in the late sixties, (29) but this company has since dropped out of fuel cell research.

Although many technological and economic barriers must be overcome, fuel cells appear to have a promising future for utility power. Small (10-40 KW) autonomous generating plants using natural gas and air have been tested by United Technologies in over 35 separate installations and have produced approximately one million kwh of electrical power. (15) The General Electric solid polymer electrolyte cells could conceivably be used in large load-leveling systems - operating to hydrolyze water during periods of low demand and in a fuel cell mode to provide power during demand peaks. Primary power generation on a large scale may soon be available with molten carbonate systems. Such a system using methanol derived from coal and air could provide utility power at unprecedented efficiencies with few pollution problems.

Finally, fuel cell systems offer an alternative power source for submersibles. Past developments and present prospects for this will be the subject of the next sections.

B. The Development of Fuel Cell Systems for Submersible Power.

Shortly after their successful development for space exploration, fuel cells began to receive serious consideration for submersible power.

As early as 1965, a fuel cell power system was installed in General Dynamics' <u>Star 1</u>. A schematic of this system engineered by Allis-Chalmers, is shown in Figure 3.1.

Hydrazine and potassium hydroxide electrolyte were mixed and circulated through the cell while oxygen gas was admitted to the cathode. Although the details of this cell's operation are now know, product water was apparently retained with the electrolyte-fuel mixture. Pressure in the system was maintained at ambient sea pressure by retaining nitrigen gas evolved in the reaction. After tests, lead-acid batteries were re-installed and a few years later, <u>Star 1</u> was retired. (3)

Another early experiment with fuel cell power in undersea application, although not for a manned submersible, should be mentioned. A United Technologies' system, similar to that used in Apollo space capsules, was used in 1969 to power a stationary underwater habitat at 50 ft. of depth near Palm Beach, Florida. The 5-KW $\rm H_2-O_2$ system weighed 100 lbs, used 100 psi bottled gas, and supplied power for 43 hours. (34)

A major U.S. government effort to develop fuel cell propulsion for submersibles began with a report on future undersea energy systems from the National Academy of Stience in 1968. (6) This report recommended concurrent research and

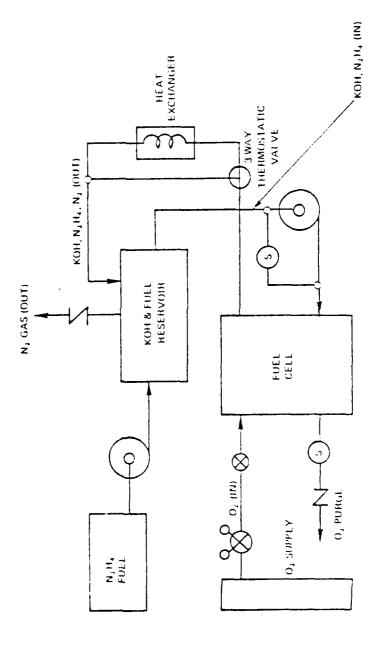


FIGURE 3.2 STAR 1 FUEL CELL SYSTEM

development of fuel cells and closed cycle dynamic engines for medium endurance (to 30 days) energy sources in the 1-100 kW range. Beginning in 1969, United Technologies (then Pratt and Whitney) began extensive studies for fuel cell power systems for the planned Deep Submergence Search Vehicle (DSSV). Two basic systems were evaluated in detail - an encapsulated Ho-Oo system and a pressure-balanced system using hydrazine and hydrogen-peroxide. Although the projected pressure balanced system was conceeded to promise, better overall performance, primarily due to minimal weight and volume impact, the encapsulated system presented less technical risk and was chosen for development. (20) The final result of this program was the production in 1971 of the PC-15 submersible power plant. The DSSV project was eventually abandoned, and the PC-15 plant underwent evaluation for installation on the DSRV, and, finally, in 1978 was installed on Lockheed's Deep Quest. The PC-15 is presently the only known fuel cell system actually being used at sea, and it will be discussed in detail in the following section.

One other fuel cell system has been tested in submersible applications. In 1970, a small Alsthom hydrazine-hydrogen peroxide system was mounted externally to the SP350 "Diving Saucer" operated in Marseille, France by the Center for Advanced Marine Studies. This small cell was loaded to 2 kW by lighting and operated in a sheltered location to 82 meters. This basic system was later expanded into 10 and 100 kW

packages which will be described under hydrazine cells in the next section.

Several other fuel cell systems have been proposed or partly developed, only a few of which will be mentioned here. In the late sixties, the Swedes began building an $\rm H_2-O_2$ system for a military submarine. Their design would have used ammonia as a source of hydrogen and cryogenic storage for oxygen, but development was discontinued following accidents in shore-based testing. (30) Presently, the Canadian and West German governments are investigating fuel cell systems for small (approximately 1,000 tons) military submarines. (33)

C. Present Alternative Fuel Cell Systems.

With extensive research and development several different classes of fuel cells could probably be engineered for submersible power systems. Here, only a few specific systems that are presently available or that have demonstrated strong potential for past applications will be explored.

1. H_2 - O_2 Systems. Available H_2 - O_2 fuel cells were primarily developed for the U.S. space program. They have many advantages for submersible power including high efficiency, high energy density, an easily handled reaction product (H_2O) , and high reliability. On the other hand, they are presently expensive and the reactants, although easily obtainable, are difficult to store on a small submersible. Two basic systems will be

described - the complete PC-15 power plant and the solid polymer electrolyte fuel cell. Additionally, alternative reactant stowage methods will be surveyed.

a. The PC-15 Fuel Cell Power Plant. The general characteristics of the PC-15 power plant are listed in Table 3.2. Although it is a direct descendent of the Apollo alkaline cell, the PC-15 was engineered with less emphasis on reduced weight, increased operating time between maintenance, and simplified support requirements.

The PC-15 consists of two major subassemblies: the power section and the accessory section.

The <u>Power Section</u> consists of unitized electrode assembles (UEA) which are electrically connected in series. A schematic of the basic UEA is pictured in Figure 3.3 The basic cell consists of anode and cathode screens separated by an asbestos matrix containing electrolyte. Each cell is approximately 13 in. square and 76 mils thick. A sintered nickel reservoir plate is adjacent to the anode, and the reservoir plate and basic cell are unitized in a structural frame of epoxy resin and fibereglass.

The UEA's are isolated from one another by three types of separator plates. A combination plate is installed between every other UEA and admits

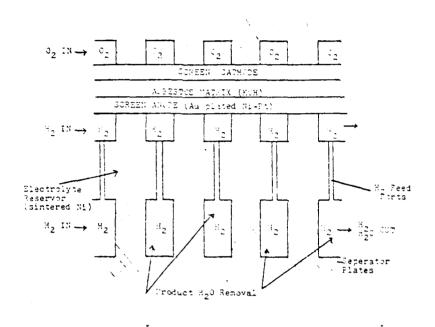
TABLE 3.2

PC-15 POWER PLANT

Rated Power	20 kW 3 100 to 140 Vdc
Maximum Overload in Thermal Equalibrium	30 kW @ 100 to 140 Vdc
Peak Power (Motor Starting)	50 kW 3 90 Vdc
Weight	391 lbs
Size	14 in. diameter x 72 in. long
Allowable Altitude	45° continuous 60° for 5 min. 3 10 kW
Start-up	20 minutes
Active Standby (Capable of 30 kW instantaneous load)	Unlimited
Shut-down	Instantaneous
Reactant Consumption	.8 Pounds/kwh
Electrolyte	32% KOH
Pressure	60 psia
Temperature	65°-110°C

FIGURE 3.3

BASIC ELECTRODE ASSEMBLY FOR PC-15 POWER PLANT



hydrogen to the anode of one cell and oxygen to the cathode of the adjacent cell, while between alternate cells there are individual $\rm H_2$ or $\rm O_2$ separator plates. The hydrogen side of these plates is also used for coolant circulation and product water removal. The separator plates are machined of magnesium and gold plated for low contact resistance and corrosion resistance.

When the UEA's and their separator plates are assembled, openings around the periphery of each unit line up to form internal manifolds which

distribute reactants and coolant to the machined passages in the plates.

The PC-15 consists of 120 cells and associated separator plates compressed between two stainless steel end plates with insulated titanium tie-rods. The separator plates at each end of the unit have extensions for external power cables, and one end plate has openings which line up with the internal manifolds and interface with reactant and coolant systems in the accessory section.

The Accessory Section - a general schematic of the PC-15 system is pictured in Figure 3.4.

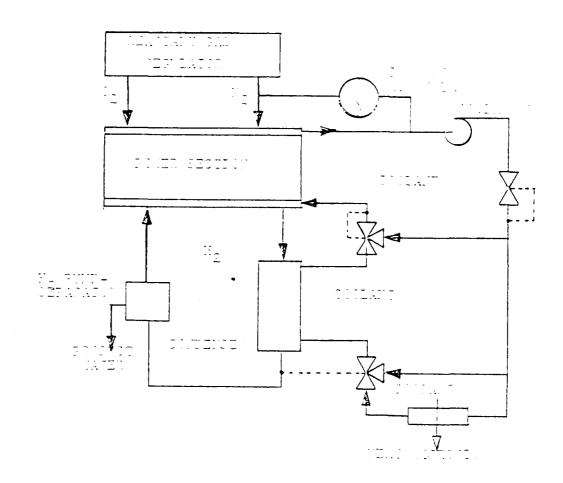
A reactant gas regulator maintains gas pressure at the electrodes at approximately 60 psia under all operating conditions. Oxygen pressure is kept slightly higher to insure diffusion will not result in water in the oxygen side.

Hydrogen and water vapor are circulated at $14 \, \mathrm{ft}^3/\mathrm{min}$ by the motor-driven pump-separator. Water is condensed, separated, and pumped to storage.

A motor driven coolant pump circulates dielectric fluorocarbon coolant through the power section, the condenser, and an external heat exchanger. A valve downstream from the pump controls flow according to coolant temperature, and two three-way

FIGURE 3.4

THE PC-15 POWER PLANT



valves maintain power section and condenser temperature by mixing coolant from the power section and the heat exchanger. Temperature schedules of the thermostatic valves are coordinated to maintain temperatures so that water is removed from the system at the same rate at which it is produced. A coolant accumulator provides an expansion volume for changes in coolant density due to temperature variations and due to compression of the external heat exchanger with depth.

Other major components of the accessory section are:

- .. An inverter providing 400 hz, 3-phase, 115 V. power for pumps and 28 Vdc for electrical control elements.
- .. An internal control unit which monitors operating conditions and power output, controls cell heaters, and includes automatic shut-down curcuits.
- .. Electrical heaters providing 4.7 kW for start-up heat and 1 kW to maintain operating temperatures at low power levels.

As described above, the PC-15 needs only pressure containment, hydrogen, oxygen, piping, and external controls to provide a complete fuel call power system for submersibles.

The DSRV PC-15 System. Figure 3.5 is a schematic of the fuel cell system engineered (although never installed) for the DSRV. This system

includes two PC-15 power plants encased in externally rib-stiffened cylinders of HY-100 steel.

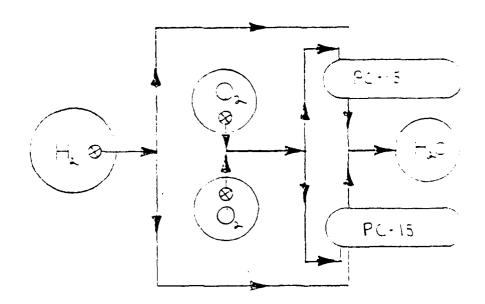
Each cylinder is 72 in. long and 18 in. in diameter.

Reactants are stored at 3,000 psi - hydrogen in one
67.8 diameter sphere of HY-100 steel, oxygen in two
33.8 in. spheres of HY-130 steel. The product water

containment vessel is a 32 in. sphere of HY-100

steel and is maintained at cell operating pressure
(60 psia). The reactant system provides approximately 700 kwh of energy. The complete system

FIGURE 3.5
SCHEMATIC OF THE DSRV POWER SISTEM



weighs 9,186 lbs. and provides 626 lbs. of positive buoyancy submerged.

A master control panel in the operator's sphere provides monitoring and manual control functions.

Deep Quest. The system installed on Deep Quest is a slight alteration of the DSRV system. Only one PC-15 power plant is installed, but reactant stowage is identical with a total of 700 kwh. As of March, 1979, Deep Quest has completed 19 separate operations with approximately 1,000 kwh of energy produced.

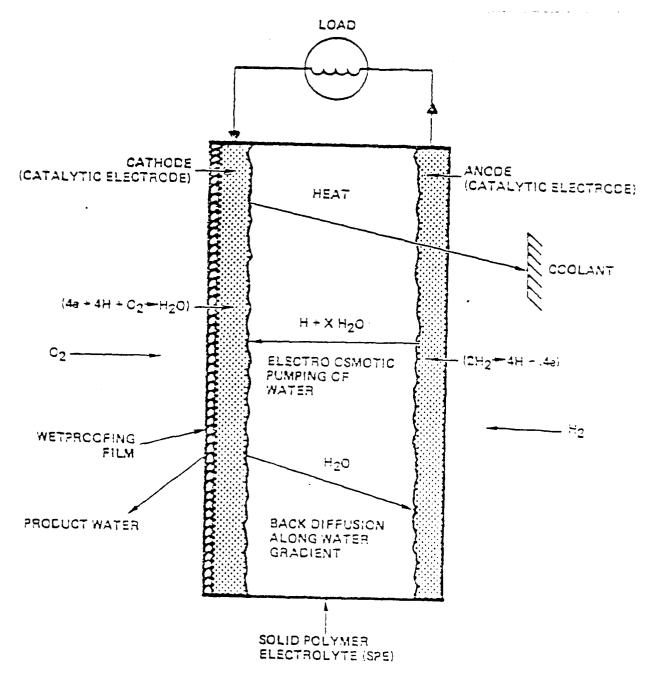
b. The Solid Polymer Electrolyte Fuel Cell. The solid polymer electrolyte (SPE), or ion-exchange membrane, fuel cell has been developed primarily by the General Electric Company in Wilmington, MA.

The principle of the SPE cell is shown in Figure 3.6. Basically, it is an acid electrolyte $\rm H_2-\rm C_2$ fuel cell in which the sulfuric acid radicals ($\rm SO_3^{-1}$) have been chemically linked and immobilized in a perfluoro linear polymer. The current electrolyte is a 10 mil sheet of polymer developed by the DuPont Corporation. Its chemical structure (simplified) is:

$$CF_3$$
 $(CF - CF - CF)$
 $(SO_3^-) (H \cdot xH_2O^+)$

FIGURE 3.6

THE SOLID FOLYMER ELECTROLYTE FUEL CELL (33)



Hydrated hydrogen ions move through the polymer chain via the SO_3^- radicals as H $^+$ ions are oxidized to water at the cathode/electrolyte interface. At operating temperatures water forms as a liquid and, in terrestrial applications, is removed by gravity. Under steady-state, the water that is ionically pumped across the membrane must be returned by back diffusion. (33)

The electrodes are metal screens embedded with platinum catalyst. The electrode screens are pressed onto each face of the SPE and a thin, porous teflon film overlays the outer surface of the cathode to prevent water film from blocking \mathcal{O}_2 admittance. (33)

Purified water is the normal coolant and flows through thin plates between cells. In present systems, one cell with its coolant channel is approximately 4 mm thick.

The single cell construction available with solid electrolyte results in several advantages in overall design:

- .. The electrodes do not have to provide any structural or containment functions.
- .. The absence of liquid electrolyte reduces corrosion, allows more latitude in differential pressure between H₂ and O₂ sides, and does not require monitoring or control of electrolyte composition.

In the past, ion-exchange membrane cells were

subject to strong degradation in performance with increasing power and had relatively low current density capabilities (15-48 ma/cm²). They were limited to comparatively low operating temperatures (25°C), and the electrolyte experienced rapid degradation which limited useful life to around 1,000 hours. The new perfluoro linear polymer, which replaced a polystyrene sulfuric acid used in the <u>Gemini</u> cells, has allowed significant improvements in all of these areas. This improvement is noticable in the developed systems listed in Table 3.3. Test cells have operated as much as 34,000 hours with no maintenance and have demonstrated sustained current densities in excess of 300 ma/cm². (33)

Although the SPE fuel cell has never been engineered into a system for submersible power, G.E. has developed a preliminary design study for a 34 kW submarine plant. The estimated characteristics of this system are shown in Table 3.4. A schematic of the proposed system would be nearly identical to Figure 3.4 for the FC-15. Oxygen rather than hydrogen would circulate with product water through the separator loop. (35)

TABLE 3.3

COMPARATIVE PERFORMANCE OF SPE SYSTEMS (33)

	Genini	NASA S kw Module	NASA Adv. Tech.
Electrolyte	Polystyrene	Perfluoro Linear	Perfluoro Linear
Design Current Density $(m\omega/cm^2)$			
Continuous	16	102	108
Poak Power	45	178	269
Operating Temperature (°C)	2.5	8.2	7 -
Module Specific Weight (Kg/kW)	32	7.3	4.5
Lite (hours)	1,000	10,000	10,000 (est.)
Cell Efficiency* at Continuous Rating	548	359	578

*Based on HHV of hydrogen

TABLE 3.4

ESTIMATED CHARACTERISTICS OF A SUBMARINE POWER PLANT BASED ON THE SOLID POLYMER ELECTROLYTE FUEL CELL

Maximum Continuous Cutput (517 ma/cm ²)	34 KW
Voltage at Max. Cont. Rating (cell voltage .53 V)	52 Vđơ
Efficiency	
at Max. Cont. Rating	463
at 10% of Max. Rating	53%
Size	40 x 40 x 80 cm
Weight	140 kg
H ₂ Flow at Max. Rating	.06 kg/kwh
Op Flow at Max. Rating	.48 kg kwh
Operating Temperature	7.4°C
Oberangua Aresante	2 atm

problem in adapting H_1-O_2 systems. A major problem in adapting H_1-O_2 systems for small supmersibles is reactant storage. Some alternative sources of hydrogen and chygen are listed in Table 3.5. Basically, there are four major alternatives - compressed gas, cryogenic liquids, liquid chemicals from which the reactants are obtained by chemical reaction, and, for hydrogen, metal hydrides. Cryogenic and liquid chemical systems have the least weight and volume impact; however, they

SOURCES AND CORPATIBLEMY OF REACTANTS FOR $\mathrm{H_2}\mathrm{-}\mathrm{O_2}$ SYSTEMS TABLE 3.5

	Wt. reactant	rin renctant	Wt reactent	KE(2). Kwh	KE(2). 11 tors(2) Kwh. Kwh.	- REACTION
OXYGEN						
Compressed 6 ₂ (3000 psi) ²	+1	.27	4.0(3)	1.36	1.25	
Liguid O ₂	-	1.14	2.0(4)	89.	.23	
llydrogen Peroxide 90%	.51	.71	2.4(5)	.82	. hυ	$^{\rm H}_2{}^{\rm O}_2$ \longrightarrow $^{\rm H}_2{}^{\rm O+1}/2$ $^{\rm O}_2$
MARCONITO						
Compressed H ₂ (3000 psi) ²		5910.	(9)16	4.13	2.75	
Liquid H2	-	.070	(4/)91	.73	49.	
Annoni a	.142	180.	8.5(5)	.39	.56	$RH_{+} + 1h = 0$
He thanol	.125	.100	9.6(5)	64.	541.	CH ₃ olf+1.5H ₂ 0+.51 0 ₂
Li thium Bydride	,25f4	.102(7)	5.5(5)	.25	34.	$c_{0_2+1.53ll_2^{0_4}1.97}$ $ll_2^{0_{11}}$
Nydrazi ne Nydrate	80.	.083	15(5)	.68	45.	п ₂ и ₂ °и ₂ 0 → п ₂ +и ₂ 0+ и ₂
Fertill, 6	510.	650.	81(8)	3.67	.85	$\text{Ferill}_{1.6} \rightarrow \text{Feri} + .811_2$
жень (5,5 иг)	820.	.065	26(8)	1.18	69.	R _C H., → M _C + H ₂

(1) system=containment+feedstock. (2)Assumes .751bs0_& .11b.H, per Kwh (PC-15 spees.)
(3) Fig.3.8.PY-180 steel, SF=4. (4) Cryogenic storage based on Ref. 23.
(5) Soft Tanks=205 liquid wt.Ref.23(5) Fig. 3.8, HY-100 steel SF=4.
(7) Assumes 50% packing (7) Fig.3.8, HY-100 steel, depth=10,000ft

present many complications in actual operation.

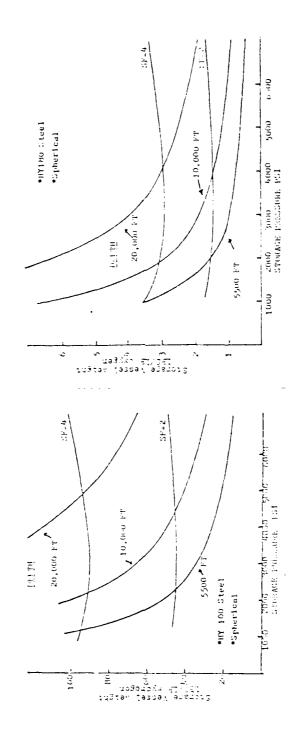
Metal hydrides can produce hydrogen either by reaction with water or, in some cases, with the addition of heat, but additional development is required for hydride systems. Compressed gas, although the least efficient alternative for specific weight and volume, is simple and available.

Reactant purity is a requirement for all storage alternatives. Inert gases will accumulate in the cell and decrease efficiency. Purging the cell is difficult at depth, and the <u>Deep Quest</u>, for example, must rise to 60 ft. for purging operations. In alkaline cells, hydrocarbons and carbon dioxide can cause cell damage. High grade commercial gas is generally suitable, and for the <u>Deep Quest</u> system provides up to 500 kwh prior to purge. (15)

1. Compressed Gas. Figure 3.7, derived from DSRV studies, indicates the major trade-offs in storing hydrogen and oxygen under pressure. At lower internal pressures, containment vessel design will be controlled by the requirement to resist external pressure. As gas pressure increases, and more gas is stored per unit volume, the amount of containment required decreases. As internal pressure increases, however, the design becomes dependent on resisting stress due to storage pressure.

PIGURE 3.7

Specific confainment for GASEOUS REACTANTS SF Ξ Salety Factor in Design for Resisting Internal Pressure



Hydrogen

Oxygen

Compressed gas storage is relatively uncomplicated and requires only pressure regulation between the stowage and power systems. Both gases are available commercially, and handling at sea does not require innovative or hazardous procedures.

Despite a reaction ratio, by weight, of 8 units of oxygen to one of hydrogen, hydrogen requires about three times more weight for containment than oxygen for two reasons. Hydrogen is 16 times less dense, and it cannot be stored in very high strength steel due to hydrogen embrittlement.

- 2. Cryogenic. Cryogenic storage of both reactants is used extensively in space systems; however, logistics, safety, environmental compatability, and cost would be difficult problems in adapting it generally to small submersibles.

 Reference (6) discusses the problems and advantages of cryogenic systems.
- 3. Chemical Systems. For submersibles, materials which can be stored in light, pressure compensated tanks offer minimum overall containment impact and, for most liquids, nearly neutral buoyancy. Unfortunately, known reaction systems providing hydrogen and oxygen require complicated or unproven subsystems for reaction and treatment or stowage of reaction products.

- (a) OXYGEN. Hydrogen peroxide (H_2O_2) storage for oxygen was investigated in the feasibility study for a pressure-balanced system for the DSSV and has been suggested in several studies. It can be decomposed in a catalytic reactor operating at ambient deep sea pressures. (36) Because the decomposition is exothermic, the product O_2 and water vapor leave the reactor at high temperature $(700\,^{\circ}\text{C}$ for the DSSV), and subsystems must be provided for cooling, condensing, and removing water.
- (b) EYDROGEN. Ammonia (29) and methanol (37) have been investigated as chemical sources of hydrogen for military submarines; however, the processes required for the conversion of these compounds would be difficult to adapt for small submersibles.

Urbach and Woerner $^{(36)}$ suggest metal hydridsea water reactions as a source of hydrogen. In a system tested to 241 bars, a laboratory-sized Kipp generator using lithium hydride and sea water yielded hydrogen exceeding 92% of theoretical values. The proposed system would use ambient pressure containment, and with $\rm H_2O_2$ as the oxygen source would provide a reactant system with a total specific weight of 1.075 kg/kwh.

4. Metal Hydride Systems for Hydrogen Storage.

Metal hydrides with relatively low heats of formation may offer a near-term method for convenient storage of low-pressure hydrogen.

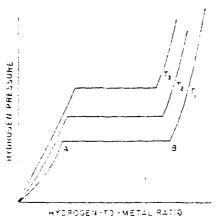
The metal systems react reversibly with hydrogen as follows:

$$\frac{2}{x}$$
 M + H₂ = $\frac{2}{x}$ MH_x

During the hydriding cycle, illustrated by Figure 3.3, hydrogen is first absorbed into the metal to form a solid solution. At saturation (A), a hydride phase with composition B is formed. With

FIGURE 3.8

IDEALIZED HYDRIDE SYSTEM



further addition of hydrogen, more of the solid phase attains composition B, and, in the systems of interest, heat is evolved. At a fixed temperature the pressure remains constant across the two-phase region from A to B, and this plateau is called the dissociation pressure of the hydride. If hydrogen is withdrawn from the system in this range, decomposition occurs until the pressure is re-established. During operation, heat must be added to the hydride system, and during re-fueling heat must be removed.

Several different hydride systems have been investigated. (38) The two listed at the bottom of Table 3.5, iron-titanium and magnesium with 5% nickel, are two especially promising systems; the former where high weight is not a limiting factor, the latter for mobile applications. The heavier

Fe-Ti system requires much less heat input $(7,250 \, \mathrm{BTU/lb.~H_2})$, and typical dissociation pressures are about 1.5 atm $\mathrm{H_2}$ at 0°C and 7 atm at 40°C. The magnesium system, on the other hand, requires 16,650 $\mathrm{BTU/lb~H_2}$ and must operate above 300°C at 1.5 atm $\mathrm{H_2.}^{(38)}$

Much practical engineering would be required to adopt these systems to small submersibles. The Fe-Ti system, which promises to be especially simple in operation, would weigh as much or more with heat exchangers and controls as 3,000 psi hydrogen storage. It would occupy nearly three times less volume, and could provide a very attractive system for volume limited military submarines.

- 2. Hydrazine Systems. The advantages of liquid reactant stowage for submersibles has been discussed previously. Hydrazine $(\mathbf{N_2H_2})$ fuel cells represent the most successful use of cells in which the fuel is dissolved in the electrolyte or delivered directly to the anode as a liquid. Ammonia, methanol, propane, and butane are other fuels that have been investigated for direct use; however, none of these alternatives have been developed into a complete system suitable for submersible propulsion.
 - a. The Hydrazine Fuel Cell. The overall reaction for hydrazine in alkaline electrolyte is:

$$N_2H_4+4 OH \longrightarrow N_2+4H_2O+4e^-$$

The exact reaction is not fully understood and several reaction mechanisms have been suggested. (29) Despite higher theoretical values using proposed mechanisms, the measured electrode potentials of hydrazine cells are nearly equal to that of hydrogen in the same media. Alkaline electrolytes are preferred for hydrazine systems (because of direct reactions with acids), and effective electrocatalysts include platinum, cobalt, nickel, and nickelboride.

For hydrazine-oxygen cells, the cathode reaction does not differ essentially from $\rm H_2-O_2$ systems. For cells using hydrogen peroxide as oxidant, the general cathode reaction is:

Silver is an effective catalyst for peroxide decomposition. The open curcuit voltage for hydrazinehydrogen peroxide cells is approximately one volt.

Although theoretical coulombic efficiencies (\cap_1 in Appendix 2) for hydrazine cells are above 99%, the overall efficiencies of actual systems are low compared to $\mathrm{H_2-O_2}$ cells. Inefficiencies in hydrazine-oxygen cells arise from self-decomposition of hydrazine, from cross diffusion of the oxidant

and fuel, and from purge losses in the oxygen side. Constant purging is required to remove nitrogen gas formed by direct reaction with diffused hydrazine. An advanced hydrazine-oxygen cell investigated by Urbach and Woerner (36) had an overall efficiency of 40%. Systems using direct hydrogen peroxide introduce further inefficiency due to decomposition of the oxidant to oxygen gas and water, and the Asthom system discussed below has an overall efficiency near 20%.

A pressure-balanced hydrazine-oxygen (cxygen provided by peroxide decomposition) system was tested for the <u>DSSV</u>. On simulated ascent from depth, supersaturated N₂ came out of solution and blocked reaction sites on the electrodes, decreasing cell effectiveness. This problem was solved in two subsequent systems. In the Asthom system, rapid recirculation of electrolyte sweeps gases cut of the cell, and in a U.S. Navy test cell, low concentration hydrazine is admitted to the back of the anode reducing nitrogen transport to the inter-electrode space, and an open structured cathode allows rapid egress of nitrogen that does get through.

Hydrazine is considered hazardous due to its toxicity, flummability, and reactivity. Special procedures would be required for handling hydrazine

at sea. Aluminum, some stainless steels, teflon, and hydrocarbon elastomers generally exhibit good characteristics for stowage and handling of hydrazine. (20)

Perhaps the greatest disadvantage of hydrazine is its high cost. Produced commercially by the partial oxidation of ammonia, hydrazine presently costs on the order of \$45 a liter and is readily available only in small quantities.

Systems using hydrogen peroxide oxidant must also pay special penalties in terms of handling and costs. $\mathrm{H_2O_2}$ is a strong oxidizer. It can cause strong irritations to the skin and eyes, and material compatability must be carefully evaluated. Presently, 503 $\mathrm{H_2O_2}$ costs 323 a liter.

b. The Alsthom Hydrazine-Hydrogen Peroxide System. Several hydrazine systems have been proposed for submersible power, (21,23) and an early system used experimentally on Star 1 has already been examined. The hydrazine-hydrogen peroxide power system developed by the Alsthom Company in Massy, France, represents an advanced system designed specifically for submersible applications. Because it stores and uses both reactants in liquid form, it allows full operation in the pressure-equalized mode with no requirement for chemical separation of fuel

stocks outside the cell. It has been developed in 10 and 100 kW modules, and the basic system was tested at sea. Disadvantages of the system are low efficiency, expensive reactants, and limited cell life.

The basic Alsthom cell is illustrated in Figure 3.9. The electrodes are stamped out of thin (50M) stainless steel coated with catalyst, Cobalt is used for the anode; silver for the cathode. A semipermeable membrane separates the reactants. Each cell is 10 centimeters square and .5 mm thick. The electrodes and membranes are mounted in PVC frames and assembled in a bi-polar configuration as shown in Figure 3.10. The thin cells and compact construction result in very high power density. The standard 10 kW (nominal) module consists of 436 cells grouped in series connected units of 33 cells each. The module provides 410 amp. at 23 V., yet it weighs only 11 kg and occupies only 6.5 dm³. (13)

The basic operation of the Alsthem system is shown in Figure 3.11. Electrolyte is pumped through two separate loops with fuel and oxidant replenished by injection. As reactants flow across the cell, gaseous products ($\rm M_2$ in anode side, $\rm O_2$ in cathode) are kept in emulsion—like form due to electrolyte velocity and cell constrictions. On

FIGURE 3.9

BASIC ALSTHOM CELL CONSTRUCTION (18)

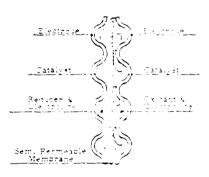


FIGURE 3.10 SCHEMATIC VIEW OF A CELL STACK ⁽³⁹⁾

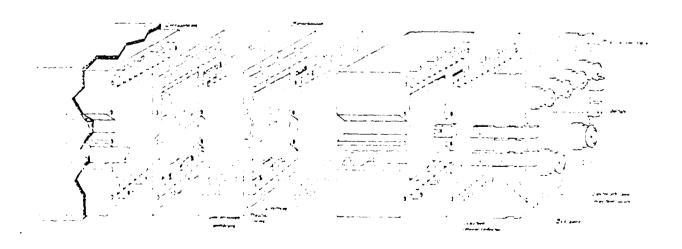
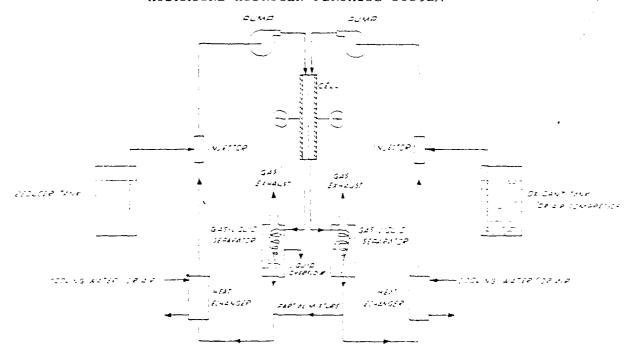


FIGURE 3.11

SCHEMATIC DIAGRAM OF HYDRAZINE-HYDROGEN PEROXIDE SYSTEM (13)



leaving the cell, gases are removed by vortex-type separators and the electrolyte is recirculated through heat exchangers. Water from direct reduction of $\rm H_2O_2$ is removed by overflow in the analyte loop.

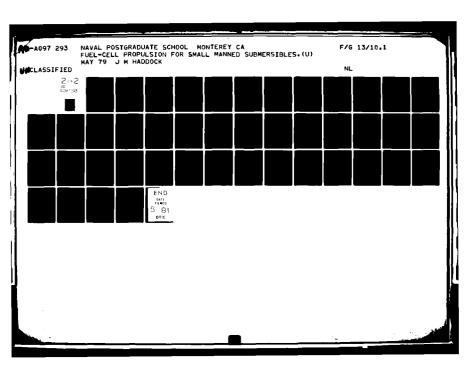
The characteristics of the 10 and 100 kW system modules are listed in Table 3.6. The 100 kW system consists of 10 cell modules identical to the 10 kW one described above. It includes all required auxiliaries and polypropylene tanks which hold 160 l. (approximately 50 kwh) of reactants.

In reported systems, cell life has been limited

TABLE 3.6

CHARACTERISTICS OF HYDRAZINE SYSTEMS

				~	92 -								
U.S. Navy Test System (2)	$M_2H_2 = (90\%)$	$0_2 \text{ (From } \text{H}_2\text{O}_2 \text{ decomp.}$	КОИ	.78 V	Single Cell				J. 08-005	.40	1.92 kg/kwh	.55 kWkg	
Alsthom 100 kW System	N ₂ H ₂ (64%)	$^{\rm H}_2^{\rm O}_2^{\rm c}$ (70%)	KOII (JM)	V 97.	115 kW (includes 5 kW for auxiliaries)	V 511	340 kg (excluding fuel)	175 cm length 47 cm diameter	7007.	. 22	3.9 kg/kwh	.34 kW/kg (Complete System)	500 hours
Alsthom 10 kW Module	282H	11,02	Koll (13)	V 01.	9.2 kW	A 8 2	11 kg	30x13.5x16 cm	0.07	.20 (est)		.84 kW/kq	500 hours
	Fuel	Oxidant	Electrolyte	Cell Voltage	Related Power	Voltage at Rated Fower	Weight	Dinenstons	Tenperature	Effections	Reaction! Consumption	Power Density	0.011 10.150



to 500 hours of operation by the formation of gas blisters in the cell membrane. (18)

D. Summary.

The chemical fuel cell is a highly efficient energy source with great potential for future employment. Except for space systems, however, fuel cell power has been used only in limited, experimental applications.

Generally, two known systems have been engineered primarily for submersibles - the PC-15 power plant and the Alsthom power modules. The PC-15 is expensive, but very efficient. It uses readily available gaseous reactants, and it has been tested extensively at sea in Deep Quest. The Alsthom system requires expensive reactants, operates at low efficiencies and has limited cell life; however, it offers uncomplicated design, very high power density, and uses liquid reactants. The only known use of the Alsthom system at sea is the 2 kW system test on the Diving Saucer.

With recent advances in ion-exchange membranes, the G.E. solid polymer electrolyte system shows great potential for several applications. At its present state of development, it could probably be engineered for submersible use with little technological risk.

Because of their various distinctive characteristics and because they are in different stages of development, comparisons of the three systems can only be done on a very super-

ficial level. The PC-15 is presently available and tested as a complete system, and it should be the basis of comparison. With its high efficiency, the PC-15 offers the most economical system in terms of reactant consumption. After development, however, a SPE system could have smaller acquisition cost, and because of its longer predicted life-time, lower overall operating costs (see Table 2.3). For the Alsthom system to be a viable alternative, cell life must be increased, and the high cost of reactants reduced.

For submersibles requiring high energy density and presently using Ag-Zn batteries, even expensive systems like the PC-15 appear to be competitive. The Deep Quest PC-15 system provides 700 kwh of energy, has a dry weight of approximately 4,000 kg, and supplies nearly 300 kg of positive buoyancy. An advanced Ag-2n battery with comparable energy storage would weigh 6,000 kg dry and would require an additional 2,500-3,000 kg of syntactic foam to achieve neutral buoyancy. Additionally, the fuel cell system allows for rapid replenishment of energy, whereas an Ag-Zn battery system requires 8-12 hours for recharge. A cost comparison of the two systems would be quite complex and would have to include factors such as the recycling of spent batteries and cells for precious metal recovery, maintenance factors, and the individual requirements for the submersible in question. For the 14-ton Canadian submersible in Reference (21), the PC-15 (evaluated as a 20 kW system) was economically superior on a

per dive basis to an Ag-Zn battery system.

The applicability of fuel cell power for a smaller submersible presently using lead-acid batteries is explored in the succeeding chapter.

CHAPTER IV A FUEL CELL SYSTEM FOR SEA CLIFF

A. Introduction

The <u>Sea Cliff</u>, operated by the U.S. Navy, has been chosen to investigate the impact of installing a "state-of-the-art" fuel cell system on a small submersible. Designed primarily for underwater engineering and salvage, <u>Sea Cliff</u> has significantly smaller energy requirements than the submarine search and rescue vehicles (DSSV and DSRV) for which the PC-15 power system was developed. Although perhaps more sophisticated in overall capability, <u>Sea Cliff</u> and her sister vessel, <u>Turtle</u>, are comparable in size (24.1 tons) and present energy capacity (45 kwh) to a number of commercial submersibles (see Table 1.1).

It should be stated that the following analysis is based on approximate calculations and is intended only to assess the overall effect of fuel cell power on Sea Cliff.

3. Present Configuration of Sea Cliff

1. General. Figure 4.1 shows a general outline of Sea Cliff, and her overall characteristics are listed in Table 4.1.

Sea Cliff and Turtle were built by General Dynamics Corporation and were launched together at New London, Connecticut, in December, 1968. Designed for underwater surveying, salvage, and general engineering, Sea Cliff

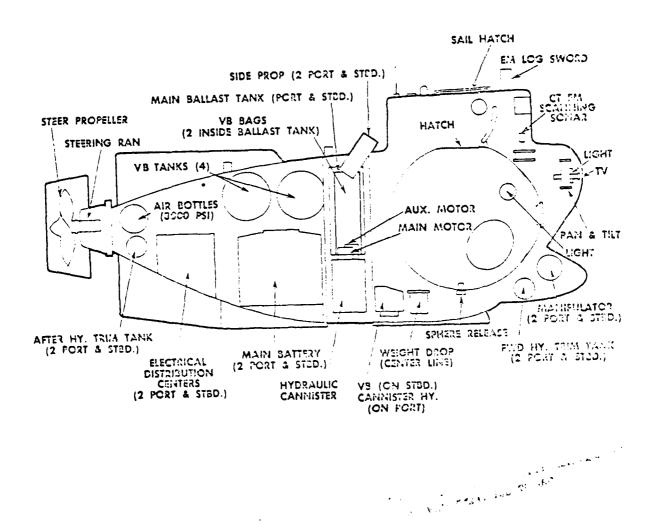


FIGURE 4.1 GENERAL OUTLINE OF SEA CLIFF

TABLE 4.1

SEA CLIFF DSV-4)

GENERAL CHARACTERISTICS

26 ft. Length: Total Energy: 45 kwh 12 ft. Beam: Speed: Max....2.5 knots/l hr 12 ft. Height: Cruise.....1 knot/8 hrs Weight (Dry): 24 tons Crew: Operating Life Support: 100 Man-hrs 6,500 ft. Interior....600 lbs Depth: Payload: (excluding personnel) Collapse 9 750 ft. Depth: Exterior....600 lbs

Pressure Hull: HY-100 steel. 1.33 in. thick, 7 ft. outside diameter.

<u>Power System:</u> 60 and 30 Vdc lead-acid batteries rated at 250 ampere hours. <u>Power is available as:</u>

120 vac, 60 hz, single phase 120 vac, 400 hz, single phase

60 Vđc 30 Vđc

(24 Vdc, 400 hz, three phase - fed directly to gyrocompass)

Emergency Power: Two 30 Vdc silver-zinc batteries and separate distribution systems located in the personnel sphere. Emergency batteries have a capacity of 12 amp-hrs at a 1 hr discharge rate.

Propulsion:

Stern. A hydraulically driven stern propeller is trainable with its shroud through 45 degrees left and right. The main hydraulic pump used for stern propulsion is driven by a 3 HP electric motor.

Side Pods. Two side pod propulsion units are powered by variable speed 60 Vdc electric motors. Side pods are connected internally by a series of shafts and universal joints and are trainable together through 360° by an electric training motor. Maximum ascent rate using side pods is 100 ft/min. Side pod motors are each rated at 4 HP.

Control. A single maneuvering control box in the personnel sphere controls speed, direction of rotation, and orientation of the three propulsors. Three modes are available: stern propeller alone, side pods alone, and all three propulsors together.

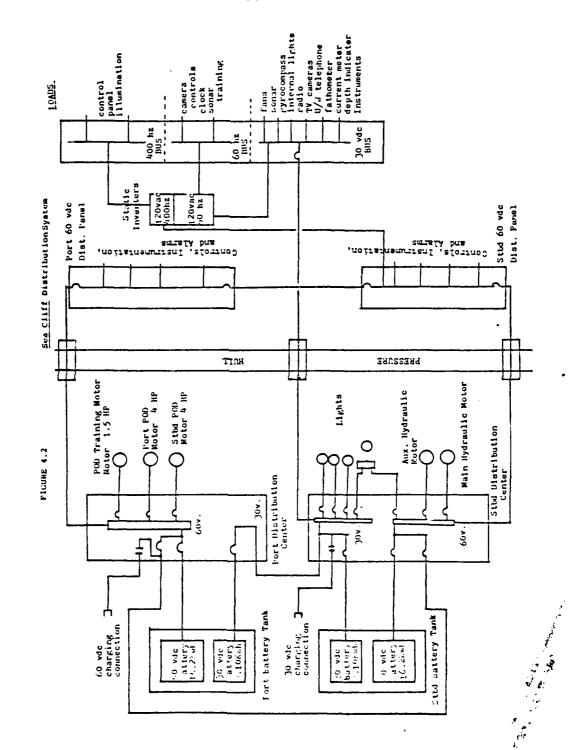
External Lights: Four 230 watt lamps, one 750 watt lamp.

is equipped with five plexiglass viewports, two external television cameras, lights, a 70 mm still camera, sonar, a gyrocompass, fathometer, and underwater and surface communications. Her two hydraulically powered manipulators can be equipped with a variety of tools including cable-cutters, drills, and grasping jaws. Tools are stored in external racks and can be interchanged during a mission. Sea Cliff presently operates out of San Diego, California.

2. Power System. Sea Cliff is powered by lead-acid batteries contained in two oil-compensated battery tanks. Each tank contains 45 cells separated into 60 and 30 volt groups. Including containment, oil, syntactic buoyance foam, and batteries, each tank weighs 4,000 pounds in air and 2,000 pounds submerged.

The installed batteries are ESB Incorporated Exide Type DMSC-llE dry-charged cells. They are rated at 250 ampere-hours at a 6 hour discharge rate (80°F) and have an estimated service life of 300 discharge cycles. Each cell weighs 43.3 pounds filled and measures 6.2x4.3x18 inches. An electrolyte scrubber (gas separator) fitted to each cell minimizes the escape of electrolyte. Nominal recharge time is 12 hours.

A general schematic of the distribution system is shown in Figure 4.2. Mormally, port and starboard cell groups of each voltage (60, 30 Vdc) are operated in parallel.



3. Operational Considerations. Presently, average dive time is about six hours with exceptional dives lasting as long as ten hours. Energy storage is generally the limiting factor in operating time, and final cell voltages are near 1.7 volts. A 100 ampere-hour reserve is maintained to ascend from maximum depth (6,500 ft.) using side pod propulsion.

According to present operators⁽⁴⁰⁾ propulsive power is adequate, and areas requiring improvement are maneuverability, manipulator dexterity, and visibility aft. It is also felt that a six hour dive is long enough for single crew operations, but that rapid turn-around with fresh operators could be valuable.

C. Proposed Fuel Cell System

Calculations and specific arrangements for the proposed system are contained in Appendix 3.

- 1. Cverall Capabilities. The following capabilities were chosen for Sea Cliff's fuel cell system:
 - a. Maximum sustained power 15 kilowatts at 60 volts. Based on running all three propulsors at full power, all lights, a 2 kilowatt hotel load, and 25% margin.
 - b. Total energy storage of 100 kilowatt hours.
 This will allow two missions at present energy
 usage rate with 10% margin. Assumed operating

philosophy of six hour single crew dives with one crew change before refueling.

- 2. Characteristics of Preliminary Design. The basic results of the design study are listed in Table 4.2.
 - a. Fuel cell system. The General Electric solid polymer electrolyte, H2-O2 fuel cell was arbitrarily chosen. Size and basic characteristics of the fuel cell are presented in Appendix 3. Calculations were based on a current density of 400 ma/cm² at maximum rated power. This is about 20% lower than sustained levels available. Increased current density would decrease the size of the active cell area required (thus reducing costs), but it would have little effect on the weight and volume of the total energy system. The overall fuel cell system would look much like the schematic of the PC-15 (Figure 3.4) with oxygen rather than hydrogen flowing with product water through the separator loop and a small compressor for pumping purged gases out of the oxygen loop. The system operates at constant purge (1.5% of O2 consumed) with inerts in the hydrogen side diffusing through the membrane to the oxygen system.
 - b. Reactant Containment System. In the preliminary design, both reactants are stored as 3,000 psi gas in spherical tanks. For the energy level chosen, the overall weight and volume of gaseous storage

TABLE 4.2 CHARACTERISTICS OF FUEL-CELL SYSTEM FOR SEA CLIFF

Maximum Sustained Power:	15 kw (60 V.)
Total Reactant Storage:	100 kwh
Output:	60 Vdc, 30 Vdc
Overall Efficiency at Rated Power:	.48
Power Module Weight	67.5 kg
Module Containment Weight	222.0 kg
Reactant System Weight (fueled)	663.8 kg
Other Weight (H ₂ O Containment, Structure)	100 kg
Total System Weight	1053.3 kg
Total System Displacement	736.9 kg
Total Buoyancy Impact	- 316.4 kg
Buoyancy Change in 100 kwh (Due to Purge)	.64 kg
Heat Rejected at Maximum Sustained Level	38,370 BTU/hr
Coolant Flow Required (H20 coolant)	792 l/hr

appears to be acceptable. Hydrogen storage in iron-titanium hydride was inestigated and, from preliminary calculations, would increase system weight by approximately 100 kg and decrease system buoyancy by more than 300 kg. At maximum sustained power, the hydride system would use one-third of the cell's waste heat for hydrogen liberation. Liquid chemical storage of reactants on a system as small as Sea Cliff would present serious technical difficulties. It is anticipated that the logistics and handling of 3,000 psi gaseous storage would be fairly straightforward.

- c. <u>Distribution</u>. For a single fuel cell module, the dual voltage system existing in <u>Sea Cliff</u> presents problems. A tentative system is shown in Appendix 3, section M, with the fuel cell module separated into two 43 cell stacks. Thirty volts is drawn from each stack and 60 volts across both stacks in series. A large imbalance in 30 volt loads for the different stacks could result in differential heating of the cell system. This might be solved by thermal isolation of the two stacks and separate cooling system controls to each group. In new design, a single direct current voltage would be preferable for a system with one fuel cell module.
- d. Arrangement. A possible arrangement of the system is shown in Appendix 3, section J. From

scaling based on Figure 4.1, it appears that the fuel cell system will fit easily into space presently occupied by the battery tanks. This arrangement must be considered very tentative as the exact configuration of <u>Sea Cliff</u> in this area is not known.

D. Impact of Replacing Lead-Acid Battery System with Proposed Fuel Cell System

- 1. Weight and Volume. Weight and displacement characteristics of the two systems are shown in Table 4.3. The net result of replacement is 1,500 kg of positive buoyancy to the vessel, which is equivalent to 2.8 tons of .68 g/cm³ syntactic foam. If lead ballast were added to overcome the positive buoyancy, Sea Cliff would still weigh approximately one ton less after the alteration. In reality, some combination of foam removal and lead ballast addition would probably accompany the battery replacement. Some fixed ballast would be required to restore stability.
- 2. Operational Considerations. The proposed fuel cell system is not complex, and it should be possible to engineer it into a very reliable power plant. A reliable fuel cell system would provide significantly higher system availability than the installed lead-acid battery.

TABLE 4.3
WEIGHT AND DISPLACEMENT SUMMARY

	Lead-Acid Battery	H ₂ -O ₂ Fuel Cell
Total Weight (Dry)	3,630 kg	1,053 kg
Total Displacement	1,814 kg	737 kg
Net Buoyancy	-1,816 kg	- 316 kg

With a two crew concept, it could more than double the useful employment time of the vessel. It is anticipated that system check-out, and energy, and life-support replenishment after two missions could be accomplished in one or two hours.

3. Costs. Only a very general attempt at cost analysis is made in Appendix 3. On a per-dive basis, considering only energy system costs, a fuel cell plant is considerably more expensive than the installed system; however, the cost of tying up a support vessel and crew for a twelve-hour battery recharge could easily compensate for the difference in energy costs. In places like the North Sea, where submersible operations are sometimes possible only a few days a month, the increased availability with fuel cell power could be extremely valuable.

E. Summary

Fuel cell power has been proposed for submersibles since the early 1960's. A 700 kilowatt-hour system is fully developed and employed on the 50-ton Deep Quest.

Fuel cell power plants are technically feasible for smaller vessels such as the <u>Sea Cliff</u>. The 15 kilowatt, 100 kilowatt-hour system considered in this study provides more than twice the energy of present lead-acid battery systems, has much less weight and negative buoyancy impact, and can be replenished in much less time. Although the fuel cell system would be more expensive in both capital and operating cost than lead-acid batteries, it does not seem unreasonable that the pay-back in terms of overall system availability would more than compensate for the expense.

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APPENDIX 1

SOME USEFUL RELATIONSHIPS AND APPROXIMATIONS FOR PRELIMINARY SUBMERSIBLE DESIGN

A. Weight and Volume

1. General. To remain at neutral buoyancy when submerged the total weight (W) of the vessel must equal the weight of water displaced by the total submerged volume (7),

$$W = \rho_{w} \nabla \Xi \Delta \tag{1}$$

where $\rho_{\rm w}$ is the density of sea water ($\rho_{\rm w}^2$ 1.027 gm/cm³ at 25°C and 1 atm) and Δ is called the submerged displacement.

In preliminary design, weight, buoyant volume, center of gravity, and center of buoyancy can be estimated for general weight groups. A typical grouping into general weight and volume categories might be:

- .. Pressure Hull (Ph)
- .. Power Plant and Energy Source (M)
- .. Payload (crew, instruments, tools, etc.) (P)
- .. Floatation Material (fm)
- .. Fixed Ballast (B)
- .. Water Ballast (BW)
- .. Auxiliary Systems (A)
- .. Outfit and Furnishings (F)
- .. Other (o)

Pressure hull volume depends on the requirements of the design. Once volume is determined, the weight of a spherical pressure hull can be approximated by:

$$W_{ph} = 23207_{ph} d/\sigma/\rho lbs.$$
 [2]

where $7_{\rm Ph}$ is in ft.³, d is the operating depth in feet and τ/ρ is the material strength to density ratio in inches. Equation [2] is from Reference (6).

Power plant and energy source weight and volume can be estimated from specific values for power and energy density and specific volume in Chapters II and III of this study (or elsewhere) once the basic power and energy levels are specified.

Payload weight and volume will be part of the specific design requirements.

Floatation for small submersibles is usually provided by syntactic foam which consists of hollow plastic or glass microspheres embedded in a resin matrix. Standard foam has a density of 42-44 lbs/ft³ and costs on the order of \$15/lb. (3) The DSRV's employ 36 lb/ft³ foam with glass microspheres. The cost of foam is dependent both on density and depth capability.

Fixed positive ballast, on submersibles of significant depth capability, would be required only in small quantities for stability, if at all. Water ballast tanks are designed to provide a specified surface draft when filled with air and neutral buoyancy for the total vessel filled with water. A separate variable ballast system must handle variations due to the density of sea water and due to system weight and center of gravity changes during a mission.

In early design stages, the other categories can be roughly estimated as simple functions of the overall displacement. Auxiliary systems, such as high-pressure air for ballast tank service, variable ballast system, life-support, and communications and control equipment, will generally make-up 5% to 10% of total vehicle weight. (4) Outfit and furnishings (hull fittings, paint) max total 3 to 5 percent of total weight. (4) For a standard working or research submarine, the "other" category, including framing and external fairing, will be on the order of 10-15% of the total weight.

Of course, these estimates must be justified in any specific design, and they would depend strongly on specific design requirements and objectives.

Overall, the sum of all weights and buoyant volumes must satisfy equation [1]; the resultant center of gravity must be below and in a vertical line with the center of buoyancy; and sufficient stability must be assured.

B. Power and Energy

1. Power. The power required can be estimated from the following relationship:

$$P_{T} = [P_{O} + K_{D} V_{R}^{3}]$$
 [3]

where: $P_O = 1$ oad other than propulsion.

 V_R = speed with respect to the water.

$$K_D = 1/2 \rho_W C_D S$$

- C_D = frontal cross sectional area drag
 coefficient
- S = frontal cross sectional area

General submersible loads are covered in Chapter II.

Often the power required for propulsion is expressed in a more general form:

$$P = K \Delta^{2/3} V^3$$
 [4]

where $\Delta^{2/3}$ approximates the effect of increasing volume on surface area, and K will depend on general hull shape.

2. Energy requirements are best determined from power spectrums for individual, anticipated missions (see Chapter II).

APPENDIX 2

NOTES ON THE EFFICIENCY OF FUEL CELLS

The intrinsic high efficiency of electrochemical systems is mentioned in Chapters II and III. Here, the basic thermodynamic definition of fuel cell efficiency will be discussed.

Background

For thermal energy conversion devices, only part of the heat energy is available for mechanical work due to inherently large entropy losses. The maximum transformation efficiency for a reversible heat engine is the familiar Carnot efficiency:

$$\eta_{\mathcal{C}} = \frac{\mathbf{W}}{\mathcal{Q}} = \frac{\mathbf{T}_1 - \mathbf{T}_2}{\mathbf{T}_1} \tag{1}$$

where W is the work done by the system, Q is the heat absorbed, and T_1 and T_2 are the initial and final temperatures (absolute) respectively. Practical considerations limit temperatures, and $n_{\rm C}$ for real machines is about 403-503. Actual conversion efficiencies (due to losses other than entropy) are on the order of 503 lower.

The enthalapy change of a chemical reaction carried out isothermally and at constant pressure (P) is:

$$\Delta H = \Delta E + P\Delta V = Q - W + P\Delta V$$
 [2]

where LE and LV are the changes in the system's internal energy and volume respectively.

If this reaction supplies heat to a reversible thermal

cycle, the only work done by the system is PAV and eq. [2] becomes:

$$\Delta H = Q$$
 [3]

Thus, the enthalapy change of the reaction is equal to the heat absorbed by the system.

If the reaction proceeds electrochemically, electrical work is also produced in moving electrons around the circuit from the anode to the cathode. Ignoring internal resistance, this work can be expressed as:

$$W_{el} = nF(V_c - V_a) = nFE_r$$
 [4]

where n is the number of electrons involved in the reaction, F is the Faraday number, $V_{\rm c}$ and $V_{\rm a}$ are the potentials of the cathode and anode respectively, and $E_{\rm r}$ is the overall cell voltage.

In the electrochemical case, then, the total work is:

$$W = W_{el} + P2V$$
 [5]

For reversible processes, heat is related to entropy changes (LS) by:

$$Q = T\Delta S \tag{6}$$

and using eq. [2] the Gibbs free energy change (4G) for a constant volume process can be expressed as:

$$\Delta G = \Delta H - T \Delta S = -nFE_{r}$$
 [7]

Isothermal (Coulombic) Efficiency

Thus, for an electrochemical cell, AG is a direct

measure of the maximum amount of net work obtainable, and an efficiency analogous to eq. [1] can be defined for reversible isothermal fuel cells:

$$\eta_{\perp} = \frac{W}{\Delta H} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$
 [8]

At a given temperature and pressure, \mathbf{n}_{i} has a definite value for each reaction system. For $\rm H_2-O_2$ cells at 25°C and one atmosphere n, is 81.3%. In some electrochemical systems with positive entropy change (C+0 \rightarrow CO) r_i can exceed unity.

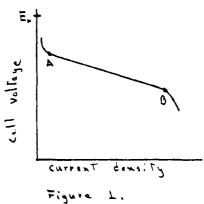
Voltage Efficiency

For actual cells under load, irreversible processes become important, and the actual voltage (E), is less than Er. The voltage efficiency is defined as:

$$n_{e} = \frac{E}{Er}$$
 [9]

The decrease in actual voltage is due to three major

kinetic effects. These effects are always present in real systems, but their relative importance depends on load levels. A plot of E vs. current density for a typical cell in shown in Figure 1. Very generally, the rapid drop in voltage to point A is mostly due to activation overpotential (V) caused by



the actual reaction kinetics at the cell electrodes. Over the linear portion from A to B, ohmic (iR) losses become relatively important, and this voltage drop is called the ohmic overpotential (V_r). Finally, at high loads, cell reactions become controlled by the rate of transport of reactants to the electrodes and a concentration overvoltage (V_c) causes a rapid decrease in overall voltage. At a given cell output actual voltage is:

$$E = E_r - (V_a + V_r + V_c)$$
 [10]

Faradaic Efficiency

The Faradaic efficiency is defined as:

$$\gamma_{f} = \frac{I}{Im} . \tag{11}$$

where I is the actual current and Im is the expected current if all reactants are consumed electrochemically. Some fraction $(1-n_{\rm f})$ of the reactants may react directly at their own electrode or with each other after diffusion across the cell. In ${\rm H_2-O_2}$ cells the Faradaic efficiency is close to unity, but in cells with less stable reactants such as hydrazine cells, it can represent a major loss.

Overall Efficiency

The overall efficiency of a fuel cell is the product of the three efficiencies discussed above:

$$r_{\mathbf{T}} = n_{\mathbf{i}} n_{\mathbf{r}} n_{\mathbf{f}} \tag{12}$$

Appendix 3

Supporting Calculations for Chapter Four.

A. Max. Sustained Power Reguired.

Propulsion: Port POD Motor 4.0 H.P.

STAL POD Motor 4.0 H.P.

Main Hydralic Motor 3.0 HP

11.0 HP = 8.2 KW

Lights: 10750 watt 30250watt 1.5 KW

Hotal (est): 2.0 KW

Margin (257.) 3.0 KW

14.7 KW

Rated at 15kw (60v.)

B. Basic cell thermo dynamics (Numbers circled are from G.E. dosign study - see Fig 3.1)

1. Voltage:

overall: $H_1 + \frac{1}{7}O_2 \longrightarrow H_2O$ $Cuthole: H_1 + \frac{1}{7}O_2 \longrightarrow H_2O$ $Overall: H_2 + \frac{1}{7}O_2 \longrightarrow H_2O$

of 25°C, 1 alm: 16, = -56.69 Kcul/mole

A Ho = -68.32 Kcal/mole

 $E_{r}^{o} = -\frac{\Delta G^{o}}{NF} = 1.229 \text{ V}.$

ΔΕ, = +5 Δ log. P mr = .014V. ΔΕς = -.027V.

Er = 1.229-.027 = 1.202 V. 16 = -55.42

2. efficiency:

$$N_{i} = \frac{\Delta C}{\Delta H} = \frac{-55.43}{-68.32} = .81$$

C. Characteristics of fuel cell module.

Requirements: 60 v.d.c., 30 v.d.c. output
15 kW max. sustained load @ 60 v.

Assume: 400 mu/un2

250 a = 400 ma/m2 = 625 m2 active cell uven

of cells 60V/.71 Vcell = 86 cells (61.06 Vactual)
wieght (4.5 x9/xw) x 15 xw = 67.5 xg.

cell dimensions: active 25 cm source
assume 2.5 cm on all edges
for support + flow chunnels

Total dimensions: 30 x 30 cm.

module dimensions o cell + cooling unit (423 cm.) Thick

86x,423 = 36.4 cm

assume accessory package 30×30×43.6 (conservative based on past designs)

total power plent: 30 x30 x80 cm.

D. Heat at max. Subtained load. (assuming $N_2=1$) $Q_{VeV} = \Delta H - \Delta G = -68.32 + 55.42 = -12.90 \text{ Kcal}_{mule}$ $Q_{VeV} = -(\Xi_{V} - \Xi) \Lambda^{\Xi} = -(1.20 - .71) \frac{96500}{7.176} = -11.30 \text{ Kcal}_{mule}$ $Q_{T} = -24.20 \text{ Kcal/mole}$

 $\dot{N}F = \frac{\# \text{ of woles}}{5 \text{ ec}} = \frac{.400 \text{ moles}}{\lambda \times 94,500 \text{ occ. me}} \cdot \frac{(25 \text{ cm}^2)}{\text{cell}} = 1.29 \times 10^{-3} \frac{\text{moles}}{\text{cell}}$ $\dot{Q}_{T} = \lambda 4.20 \frac{\text{Kcul}}{\text{mole}} \times 1.24 \times 10^{-3} \frac{\text{moles}}{\text{soc. cell}} \times 86 \text{ cell} = 2.685 \frac{\text{Kcal}}{\text{sec}}$ $\dot{Q}_{T} = \lambda.685 \frac{\text{Kcal}}{\text{Ne}} \cdot \frac{36005 \text{ ic}}{\text{Ne}} \cdot 3.97 \frac{674}{\text{Kcal}} = 38,370 \frac{674}{\text{Ne}}$ $\dot{Q}_{T} = \lambda.685 \frac{\text{Kcal}}{\text{Sec}} \cdot \frac{36005 \text{ ic}}{\text{Ne}} \cdot 3.97 \frac{674}{\text{Kcal}} = 38,370 \frac{674}{\text{Ne}}$

Heat Romoval? G= 54 udy: $\dot{Q}_{T} = 77,000 \text{ Mpc}$ $\omega = 1585 \text{ Mpc}$ $\omega = 1585 \text{ Mpc}$ $\dot{Q} = \omega \text{ Cp AT}$ $\dot{Q} = \omega \text{ Cp AT}$ $\Delta T = 12.25^{\circ}\text{ C}$ assume some AT for this unit: $\dot{Q}_{T} = 2,685 \text{ cm}^{\circ}$ $2696.3600 = \omega 10^{3} (12.25)$ calle coolent flow $\omega = 792 \text{ L/br}$

E. Reacteut Consumption:

Requirement: 100 Kwhie

Reaction at 15 kw: 1.295 x 10-3 moles H2 (From D.)

1,295 X10-> moles x86 x 3600 = 401.036 mules/h

401.036 mules/m 15 Km = 2673.575 moles

2673.6 moles X 2.01544 9/mle = 5390 grams

2673.6 mules X & (2 x 15, 494+ 5 mole) = 42,776 grams + 1,590. For purge = 43,418 grans

Had produced

5390 + 42776 = 48,166 grams

F. Reactant and Product Water Contain ment.

Ha

HY-100 steel, 3000 psi, Sataty Factor = 4 sphere
From Figure 3.:

5.310 Kg x 90 the cont = 485.1 Kg

From Hoop Strees: (Perfect gas assumption)

11.123 / 3 3000 = .0547 = x5390 4=

 $\chi_{94} l = .\chi_{44} m^3 = \frac{4}{3} T k^3 R = .413 m$ $T = \frac{\rho_T}{\lambda_C} P = 3000 \times 67$

T = 12 000 pri .413 m = .025 M

 $W = 477 R^{2} \cdot \nabla \cdot P \qquad P = 7.75 \text{ g/m/cm}^{3}$ $= 477 (41.3)^{2} \text{ x.6.5.} \text{ x.7.75} = 415 \text{ Kg}$

choose: T= 2.5 cm. R= 41.3 cm W= 485 Kg

02

H7-180 steel, 3000 psi, Sutity Futor: 4

Sphere

From Figure 3.

43.418 Kg X3 Hoscut = 130 Kg

From Hoop of the : (Perpet you arsumed)

1.429 9 2 3000 = $\lambda 9.000$ = $\lambda 9.000$ = .00343 g

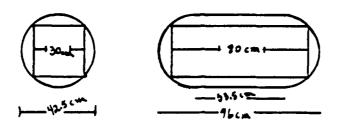
.00343 X 43,418 g = $\lambda 9.000$ = .1+4 m³

.149 m³ = $\lambda 9.000$ = .329 m

. $\lambda 9.000$ = $\lambda 180.000$ = .011 m $\lambda 19.000$ = .011 m $\lambda = 40$ (32.9) $\lambda 180.000$ = .011 kg

Choose: $\lambda = 1.1$ cm $\lambda = 32.9$ cm $\lambda = 1.30$ Kg

G. containment For Power Module



10,000 FT. & = 21.25 cm H7-100 sheet

unotified cylinder: $T_{i} = \sqrt{\frac{\rho_{i} + (1-\gamma^{2})}{\Xi}}$ $R = 30 \times 10^{6} psi$ $T_{i} = \frac{\rho_{i} + Q_{i}}{\Xi_{i}}$

 $T_{\perp} = \sqrt{\frac{4470 \, \lambda + x (1 - 5^4)}{30 \, x / 0^6}} \, \lambda 1.25 \, \text{cm} = 1.72 \, \text{cm}$

tr = 4470 x 23 cm = 1,03 cm Tr control => 2.0 cm

 $W = (\pi (3^{2} - 6^{2})) + 4\pi (3^{2} - 7) P \qquad 1 = 53.5$ $= (\pi (33.25^{2} - 31.26^{2}) + 7\pi (33.25^{2} + 7) + 77 ($

H. Volumes displacing son water

H2: No= 43.8 m V = .352 m3 = 352 (= +2.5 12.43 ft3

02: R= 34.0 cm V= . 165 m3 = 1651 = 5.81 gg3

H20: R=23.0cm V= .051 x = 51 = 1.8 ft3

Power module: ?,= 23.25 cm 1=53.5 cm V=7 2° = 1435 x2 = 143.5 L V = 5.07 6d?

I. Weight and Volume Summury:

1. Waight	add.d	
-----------	-------	--

•	WT (KG)	
power module	67.5	
H*	5.4	
٥٠	43.4	7(1)
module containment	メ メメ・0	143. 5
Ha sphere	485.0	353.0
0 2 splane	130.0	165.0
Hoo optere	50.0	51.0
Piping, cro-stauture (e	50.0	6.0
Total	1053.3 Kg	717.5 L

Displace ment: 717.5 & x 1.027 = 736.4 Kg

Net boyuncy: 736.4-1053.3 = -316.4 Kg

2. Wieght Removed.

Batterys, compensating oil, WT. 7
container 3630 Kg 1766 l

Displacement: 1766 8x 1,027 kg = 1814 kg

Not bongarcy: 3630 -1814 =+1816 kg

3. Required adjustment for neutral bouyancy.

Not change in bongony = +1816-316.4 = +1500 kg

remove syntactic From A = . 68 KJ/L

1500=(1.027-.64) = 4235.+ £=4.24 m3

W= 2980 Kg

Total wight change: 1053.3-2500-3630 = -5457kg

1 milas

add lead beliest 1500 = (11.34-1.027) V = 145.41 W= 1650 Kg Total wrapht change: 1053.3 +1650 -3630 = -926.7 Kg

- .9 70x 5

OUTIN 3

combination of from removed + whood or other weight added.

Note: Syntactic Foum P= .68 cools approx. \$7/kg.

4. Net bougency change often operation.

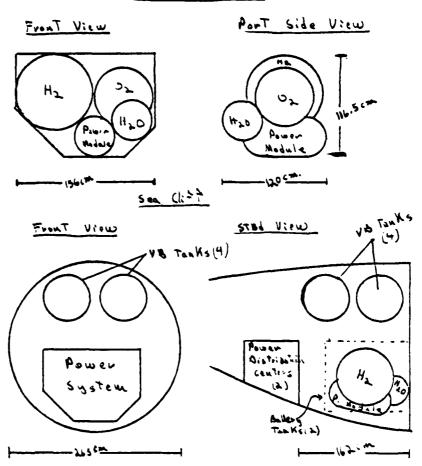
Equal to purge gases expelled (1.5% Or burned)

641.6 grams (100 Kwh of energy)

Should be easily handled by variable

bowyancy system

J. General trangement Power System



Remarks: The exact intornal averagements of Sou

Cliff are not known, and equipment or labling may

be present between the installed bettery Tanks. Governelly,

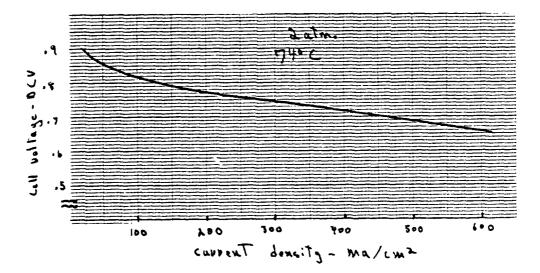
however, The Fuel cell system Fits easily into the former

bettery space. Bulleting for etability with the

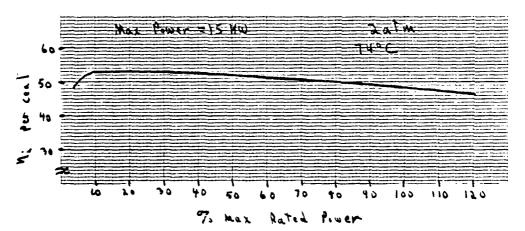
new eystem would be required.

No General Fuel cell performance.

1. cell vottage vs. Load (From GE. Study)



2. Overall officiency VS. 95 Rated Power (from G.E. Booign study)



- 3. Estimated power regained for auxilorys
 - a) Purging compression

 (air approximation, single stage compression)

 Max. depth R = \frac{304 utm}{2 u tm} = 152

 \[
 \Sigma = 16i\left(\left(1.13 Rc)^{\frac{126}{3}} 1\right) = 478.4 \text{ kp/106 = 7}\frac{3}{4uy}

 Oz rejected = 224.5 \text{ /6.667hr} \text{ (100xwh@15 kw)}

 = 28.54 \text{ f23/day}

 $\rho = 478.4 / 106 \times 28.54 \text{ kp} = 1.365 \times 10^{-3} \text{ kp} = 10.2 \text{ watts}$ where $\gamma = .7$ $\gamma = 14.6 \text{ watts}$

b) Coolect pump. $\Delta P = 75 \text{ K Pe}$ at mex power (from other 6.7. designs)

Flow at max power = $792 \text{ L/h} = .792 \text{ m}^3/\text{h}$ $KU = \frac{.792 \text{ m}^3}{3600 \text{ minser}} \times 75 \frac{\text{K:V}}{\text{M}^2} = 16.5 \text{ walls}$

assuma np= . 5 PT = 33 walls

c) 7.1d = 33+16=48 water \$\frac{50 walls}{50 walls}\$

70 of output at max rated power \$\frac{50}{15000} = \frac{1}{3}90\$

L. Alternate H2 storage.

Metal Hydrida - Fe T; H1.6 (soe chapter 3)

Wieght 5.4 Kg/H2 : .015 Cho H2 = 360 Kg

Volume 360 Kg : 3.52 x103 Kg, = .102 m

Sylverial containment

47 P,3 = .102 m3 R2 = .284 m = 30 cm

Hoop stress approximation: P= 4470 pei S= 2

HY-100 stol

T = \frac{8440(30)}{2.100.000} = 1.34 cm \frac{choose}{2.5} 1.5 cm

W = 477 (30)^2 x 1.5 x 7.75 \frac{3}{2} m3 = 131 Kg

Heat exchangers + heaters

Estimate : 100 Kg

Totals

Wieght = 360 +131 + 100 = 591 Kg

Vol. = $\frac{1}{3}$ The (31.5) = .131 m³

Disp. = $\Delta = 1.027$ V = 134.3 Kg

Heat required for hydrogen likeretion

at 7,250 ATU/LLH2

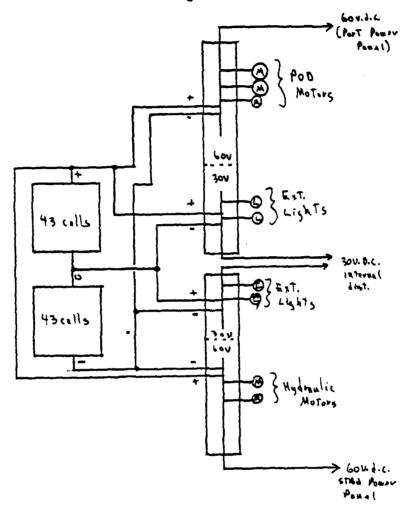
at Full power: Hz = 40 1 moles/L = 1.782 lbe/L

7, 250 x 1.782 = 12,921 BTU/L

(Total wester leeT)

12,921 = 33% of west, heat produced

M. Distribution system (tourtive)



An attempt would have to be made to balance the 30 U.d.c. loads. Although the cells could probably perform with slight variations in load between the two cell groups, serious unbalance would require separate cooling systems, or, perhaps the best solution, two separate 30 U. power plants.

No Comparative Costs [Extremely approximate]

1. Fuel Cell System (excluding dovelopment costs)

a) capital costs

Fuel coll: \$ 60,000 (reference 25)

containment: \$200,000 astimute

Total \$\frac{\beta}{260,000}\$

Assume: 150 dive (6hm)/year 10,000km cell life

2 60,000 = \$ 156 per dire

(over 11 years, discount rate not included)

b) reactant costs

Present Boston prices Hz: \$15/kg 02:35/kg
consumption / live Hz: 2.43kg 02: 19.54 kg
(45 kok 2:00)

cost/dive = 2.43 x 15 + 19.54 x .5 = 46.22 / dive

c) total cost

156 +46 = \$202.22 \$/dive

2. Battery Systems

45 Hwh

45 Hwh

1750 X 45 = 33,750

10 cycle life => \$3,375.00/dive

For 90 Hwh system => \$6,750/dive

Loud acid

\$110/Kw. hr (Reference 24)

45 Kwh

110 x 45 = 4950

200 cycle life => 4950 = #25.00 dive

